



THE ROYAL CANADIAN INSTITUTE

1-10-20















*Feb*  
*F*

# **Journal** of **The Franklin Institute**

DEVOTED TO  
  
SCIENCE AND THE MECHANIC ARTS

---

EDITED BY  
R. B. OWENS, D.S.O., D.Sc., F.R.S.C.

ASSOCIATE EDITORS :

JOSEPH S. AMES, PH.D.	COL. A. S. EVE, F.R.S.	MAJ. GEN. GEO. O. SQUIER, PH.D.
WILDER D. BANCROFT, PH.D.	W. J. HUMPHREYS, PH.D.	C. P. STEINMETZ, PH.D.
BRIG. GEN. JOHN J. CARTY, E.D	HARRY F. KELLER, PH.D.	W. F. G. SWANN, D.SC.
E. G. COKER, F.R.S.	A. E. KENNELLY, SC.D.	CHIEF CON. D. W. TAYLOR, U.S.N.
ALLERTON S. CUSHMAN, PH.D	C. E. K. MEES, D.SC.	A. F. ZAHM, PH.D.
ARTHUR L. DAY, SC.D.	RALPH MODJESKI, D.ENG.	JOHN ZELENY, PH.D.
	R. B. MOORE, SC.D.	

COMMITTEE ON PUBLICATIONS :

GEO. D. ROSENGARTEN, CHAIRMAN  
G. H. CLAMER      GEORGE A. HOADLEY      W. C. L. EGLIN      E. H. SANBORN

---

VOL. 195.—Nos. 1165-1170  
(98th YEAR)

---

JANUARY-JUNE, 1923

---

PHILADELPHIA

Published by the Institute, at the Hall, 15 South Seventh Street

1923



T

I

18

195

621384

24 10.55



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

---

Vol. 195

JANUARY, 1923

No. 1

---

## RECENT ADVANCES IN PHOTOGRAPHIC THEORY.\*

BY

C. E. K. MEES, D.Sc.

Director, Research Laboratory, Eastman Kodak Company, Rochester, N. Y.  
Member of the Institute, Associate Editor.

A PAPER, which was presented to The Franklin Institute in 1920, dealt with the structure of the photographic image and, incidentally, with the structure of unexposed photographic materials. Since that time, the structure of the sensitive material itself has been investigated by a number of workers, and the work has proved most fruitful in the increase of our knowledge of the properties and behavior of photographic sensitive materials. Already much light has been thrown on the nature of sensitiveness itself and on the behavior of the silver salts when they are acted upon by light.<sup>1</sup>

One of the greatest problems in all photographic science is the theory of emulsion making; that is, the discovery of the systematic relations which must exist between the methods employed in the preparation of the emulsion and the photographic properties of the material obtained. Attempts to solve this problem have

---

\* Presented at a joint meeting of the Sections of Physics and Chemistry and Photography and Microscopy held Thursday, December 7, 1922. Published as Communication No. 165 from the Research Laboratory of the Eastman Kodak Company.

<sup>1</sup> A review of the present state of the subject, dealt with in this lecture, has recently been published in the JOUR. FRANK. INST., by Wightman, Trivelli and Sheppard ("Studies in Photographic Sensitivity," JOUR. FRANK. INST., 194, 1922, p. 485) and I am indebted to them for many suggestions incorporated here.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.

VOL. 195, No. 1165—I

I



led to the subdivision of the subject into three separate studies: (1) The physico-chemical relations between the concentration, temperature, and other conditions existing during emulsion making, and the nature of the precipitate obtained; (2) the analysis of the precipitate into grains of different sizes; (3) the correlation of the frequency curves for the size of the grains of the emulsion with the photographic properties of the emulsion itself. Work on all three branches of the problem is now well under way.

The study of the physico-chemical relations on which depend the form in which a precipitate is produced has been developed by a number of workers in recent years, and its application to the precipitation of silver halide has been studied by Trivelli and Sheppard, their work being published in a monograph on the silver bromide grain.<sup>2</sup> In the course of this paper, it is desired to present some of the results which have been obtained in connection with the analysis of the different sizes of grain which occur in emulsions. The correlation of the frequency curves with the photographic properties of the emulsion itself has already been dealt with by Wightman, Trivelli, and Sheppard, and will probably not present much difficulty when the nature of the frequency curve is more fully understood, and we may therefore expect that before long we may be able to define the form of the precipitate of silver bromide which will produce given photographic properties in the emulsion. An effective control of emulsion making will, of course, involve much study of the conditions of precipitation and also of the properties of the gelatine, which, apparently, has a very great influence on the specific sensitiveness of the silver halide produced.

For many years the nature of the product of light action upon silver halide, which is generally known as the "latent image," has been the subject of speculation and discussion, but the work which has been done upon the individual grains which compose the sensitive surface of a photographic material enables the nature of the latent image and its production to be attacked from a new angle, which must be valuable in shedding light upon this classical problem. The chief workers in this field are in three different countries. Professor The Svedberg, of the University of

---

<sup>2</sup> Trivelli, A. P. H., and Sheppard, S. E., "The Silver Bromide Grain of Phot. Emulsions," Eastman Kodak Company, Rochester, N. Y.



Upsala, Sweden, published the first paper in 1919.<sup>3</sup> This dealt specifically with the influence of the grain structure upon sensitiveness. In 1918, there was formed in England a research association for the photographic industry, the first director of which was R. E. Slade. He and his colleagues, G. I. Higson and, later, F. C. Toy and W. Clark, have published a number of papers on the subject.<sup>4</sup> In the research laboratory of the Eastman Kodak Company, when Svedberg's paper appeared, A. P. H. Trivelli<sup>5</sup> had already been at work for some time studying the microscopic structure of emulsions, and with his colleague F. L. Righter has now published several papers. At the same time E. P. Wightman and S. E. Sheppard<sup>6</sup> have attacked the problem and within the last two years L. Silberstein<sup>7</sup> has done a great deal of work on the mathematical analysis of the questions involved.

In his earlier work Trivelli made a large number of photomicrographs of emulsions taken from standard photographic plates and films, one of which is reproduced in Fig. 1.

It will be seen that the silver bromide grains, of which the emulsion is composed, are of extremely varied sizes, there being present a large number of small grains, down to the limit of those visible with a microscope, and a smaller number of large grains, including some of very much greater area than the smallest grains present. The largest grains are all polygons with angles of  $60^\circ$  and  $120^\circ$ . There is a tendency to round off the corners and edges of the small grains, so that the smallest grains appear to be more or less spherical.

---

<sup>3</sup> Svedberg, The, "Körngrosse und Empfindlichkeit in Photographischen Emulsionen," *Z. Wiss. Phot.*, **20**, 1920, p. 36.

<sup>4</sup> Slade, R. E., and Higson, G. I., "Photochemical Investigations of the Photographic Plate," *Proc. Roy. Soc.*, **98A**, 1920, p. 154.

Higson, G. I., "The Action of Light on the Photographic Plate," *Phot. J.*, **45**, 1921, pp. 35, 144.

Toy, F. C., "The Sensitivity of Silver Halide Crystals which are Geometrically Identical," *Phot. J.*, **45**, 1921, p. 471.

<sup>5</sup> Sheppard, S. E., and Trivelli, A. P. H., "Note on the Relation between Sensitiveness and Size of Grain in Photographic Emulsions," *Phot. J.*, **45**, 1921, p. 400.

<sup>6</sup> Wightman, E. P., and Sheppard, S. E., "Size-Frequency Distribution of Particles of Silver Halide in Photographic Emulsions and its Relation to Sensitometric Characteristics, I and II," *J. Phys. Chem.*, **25**, 1921, pp. 181, 561.

<sup>7</sup> Silberstein, L., "A Quantum Theory of Photographic Exposure," Part I, *Phil. Mag.*, **44**, 1922, p. 257.



A study of these small spherical grains by R. B. Wilsey,<sup>8</sup> however, using the methods of X-ray crystal analysis, shows that even the smallest grains are still definitely crystalline and have the same structure as the large grains, the crystalline form being a cubic lattice. The shape of the large grains is very well illustrated in Fig. 2, which shows a special emulsion prepared to give a large proportion of relatively large grains.

The fact that the grains in an emulsion are of many different sizes has been known for many years, and in 1915 in a paper presented to The Franklin Institute entitled "The Physics of the Photographic Process,"<sup>9</sup> attention was called to the fact that the sensitiveness will depend upon the distribution of different sizes of grains, as will also the shape of the plate curve, this curve being the relation between density and logarithmic exposure. It was suggested that the shape of the curve will depend to a considerable extent on the distribution of the different sizes of grains in the emulsion. With a homogeneous emulsion we shall have a curve with a short over- and under-exposure portion, as seen in Fig. 3, and by adjusting the sizes of grains so that there is a sufficient number of grains distributed around the mean, we can diminish the under-exposure portion to obtain a longer straight line (Fig. 4). We can therefore form a mental picture of the relation between the distribution of the grain and the sensitiveness curve.

It will be seen from this that as long ago as 1915 it was realized that the distribution of the different sizes of grains in an emulsion might play a very important part in determining the characteristics of that emulsion. The problem was to measure the distribution of the grains; that is, the number of grains of a given size which occurred in an emulsion and the variation of the number with the size of the grain. This is a problem which has often arisen in scientific work. It has been studied in connection with suspensions of all kinds.<sup>10</sup> Various indirect methods of attacking the problem have been suggested. It is possible to get determinations by settling the emulsion, taking advantage of the fact that the larger particles will settle most rapidly according to Stokes' law.

---

<sup>8</sup> Wilsey, R. B., "The Crystal Structure of Halides," *Phil. Mag.*, **42**, 1921, p. 262.

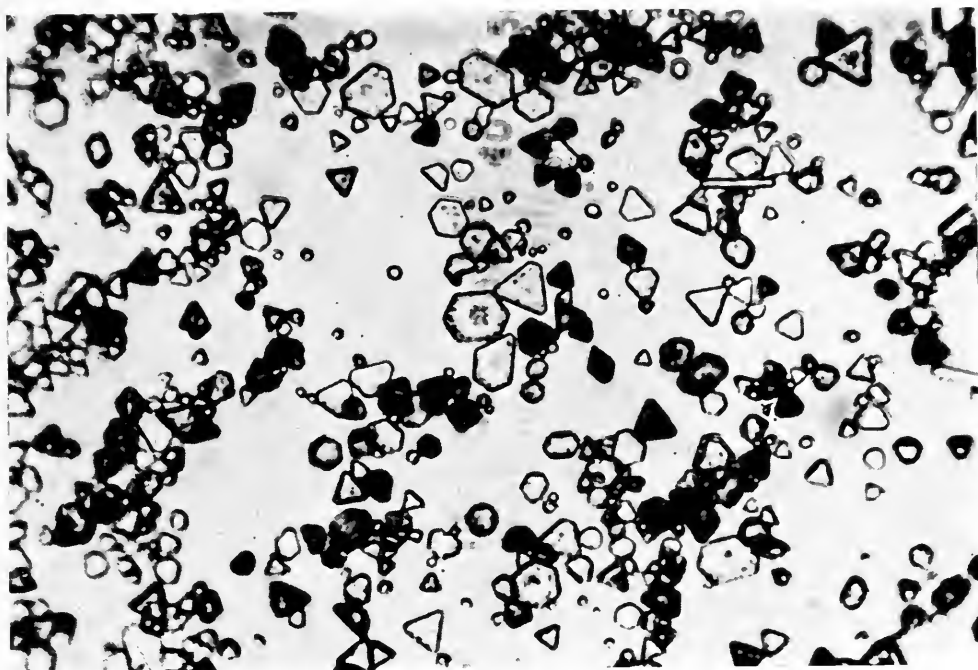
<sup>9</sup> J. FRANK. INST., 179, 1915, p. 141.

<sup>10</sup> "A Photomicrographic Method for Det. of Particle Size of Paint and Rubber Pigments" by Henry Green, N. J. Zinc Co., J. FRANK. INST., Vol. 192, Nov., 1921, p. 637.



This has been carried out in various ways by Odén, Westgren, and others,<sup>11</sup> but the direct method is, clearly, to spread out a thin layer of the emulsion and to count the different sizes of grains occurring in it. Trivelli accomplished this by photomicrographic methods. He photomicrographed a thinly coated emulsion at an enlargement of 2500 diameters, enlarged the negatives to 10,000 diameters, outlined all the grains of these enlargements, and then planimetered the grains and obtained tables showing the areas

FIG. 1.



Silver halide grains of a photographic emulsion.

of the different grains present, at least a thousand grains being counted for each emulsion. Wightman and Sheppard obtained the same results by the use of the camera lucida instead of photomicrography. From the tables, curves were obtained showing the relation between the size of grains and the number present for several standard emulsions. Fig. 5 shows the results for the portrait film and slow lantern emulsions: It will be seen that the curve for portrait film shows a distribution of sizes of grain which corresponds approximately to a probability curve, the maximum number

<sup>11</sup> Odén, S., *Intern. Mitt. und Bodenkunde*, 5, 1915, p. 257; *Proc. Roy. Soc., Edinburgh*, 36, 1915-16, p. 219; *Koll. Zeit.*, 18, 1916, p. 33; 26, 1920, p. 100.

Westgren, A., *Zeit. Anorg. Chem.*, 94, 1916, p. 193.



of particles being for particles of a diameter of approximately  $0.5\mu$ , the particles both smaller and larger than this being fewer, until we have very few particles indeed of larger size than  $2.7\mu$  and also few of smaller size than  $0.2\mu$ . On this small side no particles can be measured less than  $0.2\mu$  because this is the limit of the resolving power of the microscope, so that even if smaller particles exist, as they certainly do in some emulsions, they cannot be measured. Sometimes the maximum number of particles are

FIG. 2.



Silver halide grains of large size from a special emulsion.

those of very small size, and in this case the maximum is so far on the small side that no maximum can be measured owing to the limit of the resolving power of the microscope, and, instead of a symmetrical probability curve, we get one of an exponential shape. This is shown in the curve of the lantern slide emulsion.

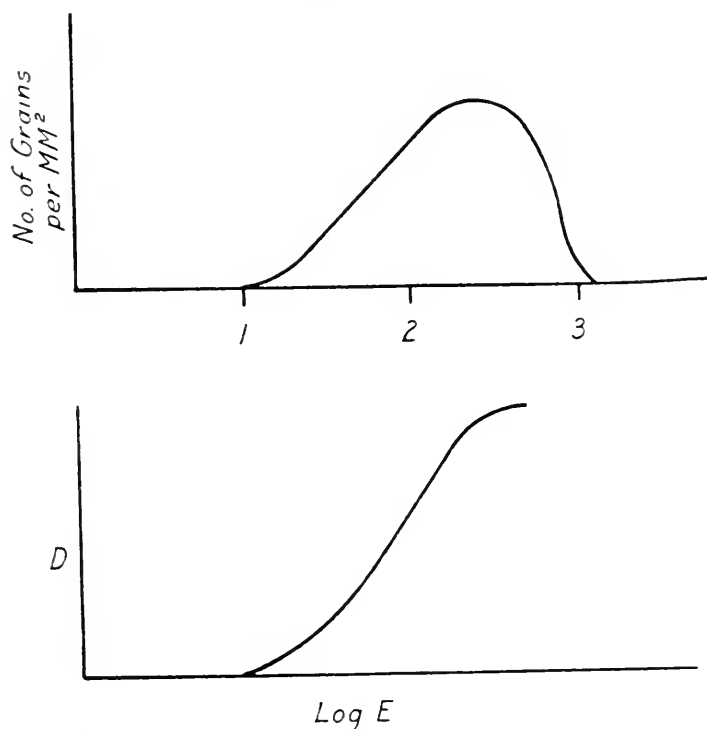
It is probable, however, that curves showing diameters will not be those of real value, because the controlling factor will not be the diameter of the particles, but their projective area, and the factor of importance in relation to their projective area is not the number, but the effective area of the particles of a given area



size, so that instead of using curves in which the number of particles are plotted against the diameter, we should rather use those in which the effective projective area of the grains of a given size is plotted against the area of the single grains; the curves for the two emulsions previously referred to are given in Fig. 6.

While this work was in progress, Slade and Higson<sup>12</sup> had studied the grain of process plates, which they thought to be very homogeneous in size, and they considered that if the grains are all

FIG. 3.



Suggested frequency and characteristic curves of emulsion.

of the same size, we get the steepest characteristic curve possible, while if the grains are not all of one size a flatter curve is obtained. They found that, in all the cases they examined, the steepness of the curve could be foretold from the photomicrographs.

Svedberg<sup>13</sup> investigated systematically the relation between the size and sensitiveness of grains in photographic emulsions.

<sup>12</sup> Slade, R. E., and Higson, G. I., "The Emulsion for a Process Plate," *Phot. J.*, **43**, 1919, p. 260.

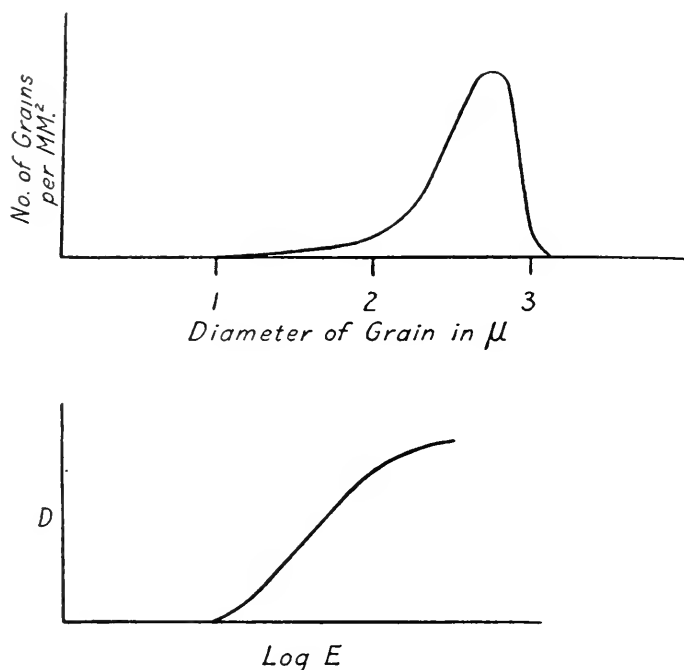
<sup>13</sup> Svedberg, The, and Anderson, H., "On the Relation between Sensitiveness and Size of Grain in Photographic Emulsions," *Phot. J.*, **45**, 1921, p. 325.

Svedberg, The, "The Reducibility of the Individual Halide Grains in a Photographic Emulsion," *Phot. J.*, **46**, 1922, p. 183.



He prepared emulsions so thinly coated that the grains were all in single layers and counted the grains of different sizes by classifying them into four classes. The emulsions were then exposed and developed and the developed silver removed, the remaining grains, representing those which had not been made developable by the action of light, being counted. In this way curves could be obtained showing the sensitiveness of the grains of each class, and it was found, as might be expected, that the larger grains were much more sensitive than the smaller grains.

FIG. 4.



Suggested characteristic and frequency curves of emulsion.

Svedberg<sup>14</sup> next suggested that the product of the light action in the halide grain, that is, the substance of the latent image, consists of small centres distributed through the grain or through the light affected part of the grain, and that these centres are distributed according to the laws of chance. A certain grain will therefore become developable if it includes one or more developable centres after exposure, and, according to the laws of chance, the probability of centres occurring in a grain can be calculated. The centres become visible during development, for if a plate be developed for a very short time, the grains show these centres as

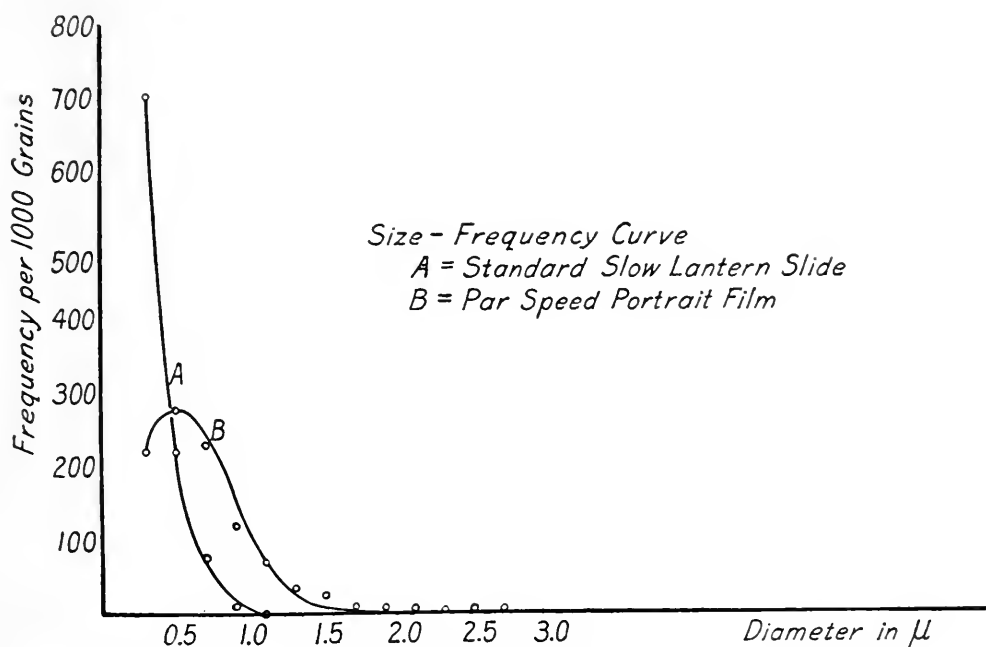
<sup>14</sup> Svedberg, The, "On the Relation between Sensitiveness and Size of Grains in Photographic Emulsions," *Phot. J.*, **46**, 1922, p. 186.



small black spots upon them. This was shown by Hodgson<sup>15</sup> as early as 1917 (Fig. 7).

Svedberg showed the centres clearly and made plain their relation to the silver bromide grains by photographing the grains before development by deep red light, then developing for a short time, and removing the undeveloped halide. On the plate, there are then left small dots, and comparison with the first plate showed these to correspond with the silver halide grains originally present.

FIG. 5.



Frequency curve (A) standard slow lantern slide and (B) par speed portrait film.

Fig. 8 showing this is reproduced here from Svedberg's paper.<sup>16</sup> In the figure, *A* represents the undeveloped silver halide grains and *B* the centres found after removal of the grains. In *C* the two figures are shown superimposed so that the centres are shown on a faint outline of the original grain.

Svedberg has shown that the number of centres produced in this way by initial development increases with the exposure in accordance with the usual photographic laws, and it might be assumed that the discovery of these centres produced during development is a proof of discreteness in the action of light upon

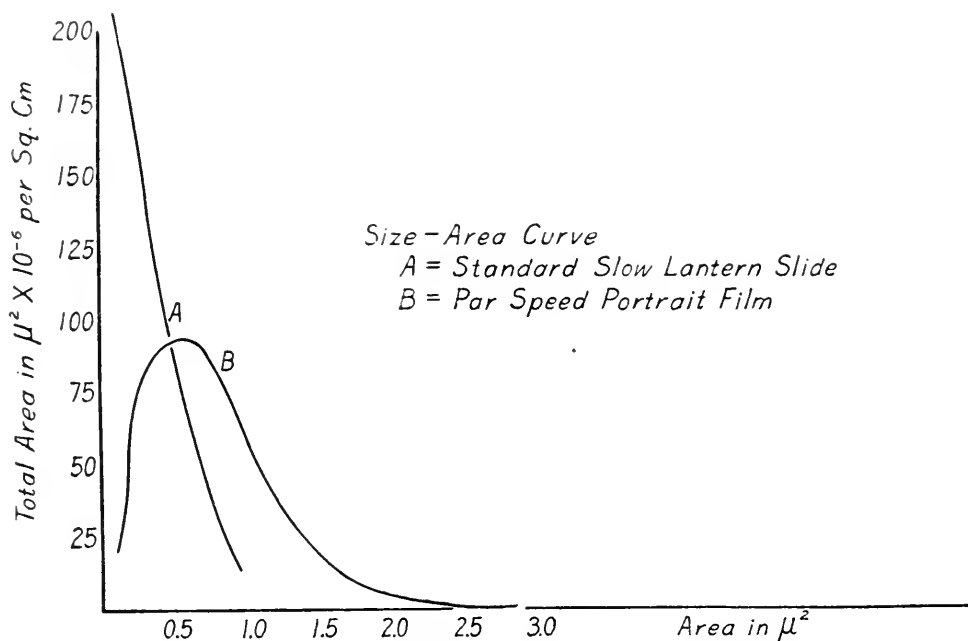
<sup>15</sup> Hodgson, M. B., "Physical Characteristics of the Elementary Grains of a Photographic Plate," J. FRANK. INST., **184**, 1917, p. 705.

<sup>16</sup> Svedberg, The, "The Interpretation of Light Sensitivity in Photography," Phot. J., **46**, 1922, p. 310.



the grain and that they must result from a structure in the silver bromide grains either existing before exposure or produced during exposure and corresponding, for instance, to spots of sensitiveness. While the evidence for this seems very great, it must be remembered that we know nothing about these centres until development takes place and that even if the whole grain were equally affected by the action of light and changed to the same extent, we should still expect development to take place first at

FIG. 6.



Size-area curve (A) standard slow lantern slide and (B) par speed portrait film.

some local spot corresponding to slight surface differences in the grain. A sheet of metal immersed in acid, for instance, will not be attacked uniformly all over the surface. Because of the impurities, action will start at individual points, and since development corresponds presumably to deposition of silver from a supersaturated solution, it would naturally occur at local spots if any form of impurity were present and would proceed first at those spots. It may be argued that the presence of such impurities in the grain would of itself produce changes in sensitiveness, but the point that it is wished to emphasize is that local initial development is not necessarily associated with local differences of sensitiveness.

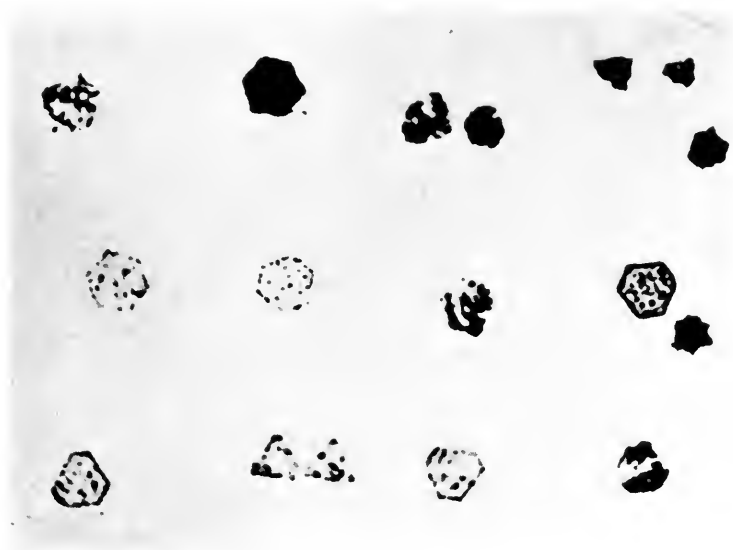
In his work on silver halide grains, Trivelli showed by his photomicrographs distinct spots of reduction produced by the



action of light before any development had been applied to the grains (Fig. 9).

On development, however, he found that the centres of reduction produced at the beginning of development did not correspond to the visibly affected spots which were produced by the action of light. These spots were distributed over the surface of the grain, whereas the initial reduction most frequently started at the edges or corners of the grain. The fact that the

FIG. 7.



Partly developed grains showing centres.

centres of development start at the edges of the grain is mentioned also by Toy<sup>17</sup> and is, of course, in accordance with what one would expect for a reaction such as development, if the edges and corners have a greater solution pressure than the rest of the surface, and thus these will be more liable to attack.

If we assume that developable centres correspond to a segregation of the latent image, then the distribution of centres according to a probability law is what we should expect, however they are produced, since a chance distribution would be most probable in the absence of any known cause leading to another specific distribution.<sup>18</sup>

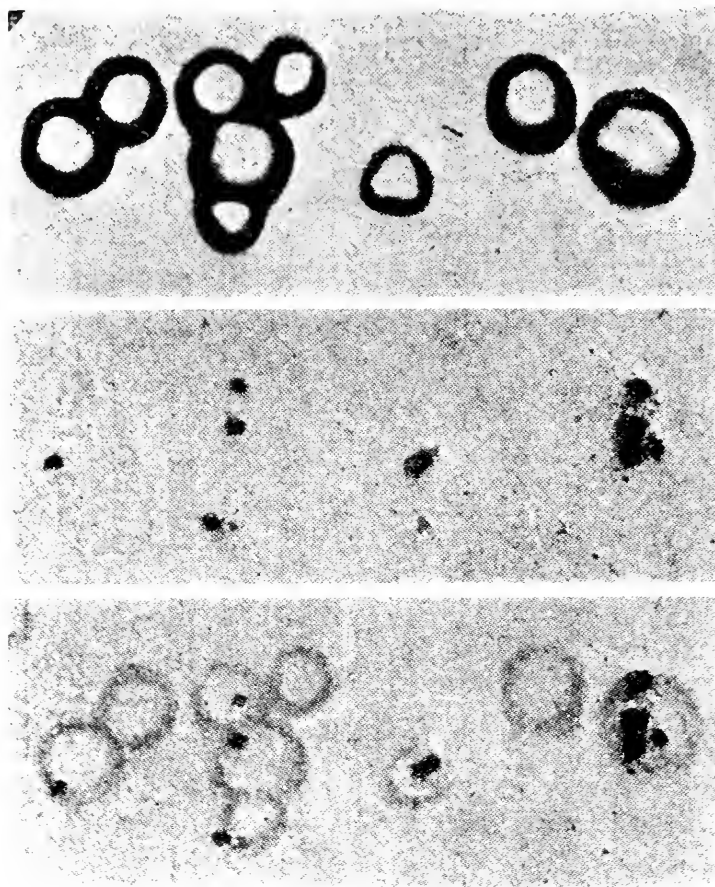
<sup>17</sup> Toy, F. C., "The Quantum Theory of Photographic Exposure: A Criticism," *B. J.*, **69**, 1922, p. 443; "On the Theory of the Characteristic Curve of a Photographic Emulsion," *Phil. Mag.*, **44**, 1922, p. 352.

<sup>18</sup> Cf. Toy, F. C., *Phil. Mag.*, 1922, p. 354, and Wightman, Trivelli and Sheppard, *loc. cit.*



In a recent paper, W. Clark<sup>19</sup> of the British Photographic Research Association has acted upon grains with a reducing solution such as sodium arsenite and concludes from his results that the centres are an essential part of the grain structure and they exist in the grains from the time the emulsion is made. The

FIG. 8.



Grains and development centres.

validity of Clark's conclusions depends upon the assumption that the centres are not produced during development but exist before it, and the fact that he gets exactly the same chance distribution by the action of sodium arsenite as for light would suggest either that the centres attacked by light are also attacked by sodium arsenite or that the centres produced on development are produced

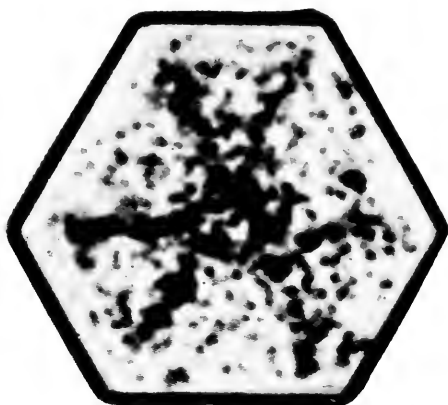
<sup>19</sup> Clark, W., "Grain Structure *versus* Light Quanta in the Theory of Development," *B. J.*, 69, 1922, p. 462.



by development and are not directly dependent upon the existence of localized changes before development.

In the very important paper by Toy, quoted above, measurements are given showing that the number of nuclei produced on initial development are proportional to the number of grains which become developable on complete development and that the larger grains not only have more nuclei on account of their size, but that these nuclei are more sensitive to light than those in the smaller grains, the sensitivity of a grain being the sensitivity of its most sensitive nucleus. Svedberg considers that the number

FIG. 9.



A silver bromide crystal deposited from solution in ammonia showing surface decomposition produced by light.

of developable centres per unit area of grain surface is a measure of the light sensitivity of the silver halide of the emulsion. From Toy's work it would seem to be doubtful whether we can speak of the light sensitivity of the halide itself in terms of the nucleus theory, since this will vary with the size of the grain.

As will be shown later, Silberstein has come to much the same conclusion as Svedberg as to the relation of the number of developable centres to light sensitivity and has given mathematical formulæ for this connection.<sup>20</sup>

Renwick<sup>21</sup> has suggested that sensitiveness is due to nuclei which probably consist of a colloidal solution of silver in the halide. He thinks that in the crystalline silver bromide there is

<sup>20</sup> Silberstein, L., "A Quantum Theory of Photographic Exposure," Part III, to be published shortly in *Phil. Mag.*

<sup>21</sup> Renwick, F. F., "Colloid Chemistry and Photography," *B. J.*, 68, 1921, p. 607.



present some highly unstable form of colloid silver in solid solution, and it is this colloid silver which first undergoes change on exposure to light. He believes that these silver particles may be negatively charged and that the action of light is to discharge them and thus enable the coagulation into larger groups of the particles of colloidal silver which existed in the grain before exposure. He believes that it is these groups of coagulated particles which are the reduction centres.

While Svedberg was studying the distribution of the developed centres among the grains and finding that they had a probability distribution, Silberstein and Trivelli<sup>22</sup> made the same discovery for the number of grains which become developable with a given time of exposure. They found that the chance of a grain becoming developable increased very much with its size and obtained an equation leading to the same results as Svedberg's for the relation between the number of developable grains and their area. Silberstein, however, who obtained his formula theoretically before the experiments of Trivelli were completed, ascribed this not to structure in the material, but to a structure in the radiation falling upon it.

Recently, a number of phenomena have been observed which are very difficult to explain by the use of the classical wave theory of light, and it seems not unlikely that it may be necessary to turn to a theory having some analogy to the corpuscular theory. As a first step towards this, Max Planck suggested his now well-known quantum hypothesis, according to which an atom radiating energy liberates it in discrete quanta, the amount of energy corresponding to each quantum being a constant multiplied by the frequency of the light. Bohr adopted Rutherford's theory of the structure of the atom, considering the atom to consist of a nucleus carrying a positive charge of electricity and to be surrounded by one or more electrons carrying a negative charge, the electrons revolving about the positive nucleus itself. He imagined that the electrons revolve without radiating but that when an electron suffers some violent shock, it gives energy, and that this energy is radiated and has the value of Planck's quantum.

---

<sup>22</sup> Silberstein, L., "Quantum Theory," Part I, *loc. cit.*

Trivelli, A. P. H., and Righter, F. L., "A Preliminary Investigation on Silberstein's Quantum Theory of Exposure," *Phil. Mag.*, **44**, 1922, p. 252.



Thus, if an electron, by the sudden impact of another electron, for instance, is thrown out of an atom and is attracted back to its place by the nucleus, then as it falls back, it will send out a pulse of energy, and it will be seen at once that if light is produced by such a behavior of electrons, it is inherently probable that it will be radiated in pulses rather than continuously. Since, according to Bohr, the frequency of the vibration emitted is exactly proportional to the energy which the electron releases, Planck's quantum condition is fulfilled, and we have the famous equation

$$I'e = h\nu$$

where

$I'$  is the voltage acting on the electron charge  $e$

$\nu$  is the frequency

and

$h$  is Planck's constant

In an X-ray tube, the discharge of electricity is in the form of a stream of corpuscles travelling with a velocity which is very high and which depends upon the voltage of the electric current applied to the tube. When these corpuscles strike the target, their energy is radiated in the form of X-rays, and we know that these X-rays partake very closely of the nature of light except that the length of the waves is about one-thousandth of those of light or, what is the same thing, their frequency is a thousand times as great. It is to this that they owe their great penetrating power.

On the classical wave theory of light, then, we should imagine that an X-ray tube having its target bombarded by the stream of corpuscles produced by the current would emit waves of X-rays spreading into space just as waves of light are imagined to spread from a source; but now comes a great difficulty. When these X-ray waves travelling out pass through a gas and are absorbed, they cause the molecules of the gas to emit electrons, and these electrons are emitted with almost exactly the same velocity as the electrons in the tube which produced the X-rays themselves. The extraordinary nature of this phenomenon is well illustrated by Sir William Bragg in a recent article:<sup>23</sup> He takes as an analogy the dropping of a log of wood into the sea from a height of one hundred feet. A wave radiates away from where it falls; the wave spreads; its energy is more and more widely distributed:

<sup>23</sup> Bragg, W., "Electrons and Ether Waves," *Sci. Monthly*, **14**, 1922, p. 153.



the ripples die away; at a short distance, a few hundred yards perhaps, the effect will apparently disappear. If the water were perfectly free from viscosity, and there were no other causes to fritter away the energy of the waves, they would travel indefinitely, always diminishing in their height. Now, at some point, say a thousand miles away, these now microscopic ripples encounter a wooden ship. We should expect that they would produce no effect, especially as they may have passed many other ships without having affected them, but, for some reason, as these tiny ripples reach the ship, a plank of the same weight as the log is hurled out of the ship to a height of exactly one hundred feet, and the whole energy which was originally supplied by the log falling into the water is concentrated upon the ejection of the plank. It will be seen at once how inadequate the wave theory is to account for this phenomenon. Similar difficulties occur in connection with photoelectricity or the liberation of electrons under the influence of light.

The method by which a photographic emulsion adds up light during a long exposure has always been a great problem when it is considered from the standpoint of the classical wave theory. If we accept the idea that the grains of silver halide in an emulsion are exposed to a continuous flood of light from a distant star, for instance, then each grain must be imagined to be integrating light until it has received enough to make it developable. Since the exposure required in astronomical photography is frequently very long, we must consider that the grains continue to integrate the light for many hours, and it is difficult to imagine any mechanism which would enable them to do this. The difficulty is enhanced by the fact that even a very brief exposure continues to produce an effect after an interruption of a long period, so that if all the grains have been affected by the first exposure, they must be capable of storing energy quite insufficient to make them developable and to hold this energy for a long period and then resume its accumulation at the level where the interruption occurs. In the same way, when we study the exposure of the individual grains, even if we could imagine some mechanism by which the grains could store up the energy falling upon them until they became developable, we should expect that all the grains of the same size would become developable at the same time unless, indeed, we assume the process of exposure to be



autocatalytic in nature. When grains are examined under the microscope, however, some of them are found to have been affected before others. If we imagine that they all have become exposed to a uniform flood of light, we must consider that these grains differ in sensitiveness among themselves and that the possibility of change on exposure, so that they become developable, is due to the presence of a sensitizer. This may either be concentrated unequally in the different grains or may form centres of sensitiveness similar to those supposed to exist by Svedberg and other workers in the field who think that the centres found at the beginning of development are the origin of sensitiveness and are present from the time of making the emulsion.

If we had no prior knowledge of the wave theory of light, however, it is clear that the simplest explanation of the sensitiveness of different grains would be that, instead of a continuous flow of light in the form of waves on to sensitive films, the light was falling upon it as a rain of projectiles and that these projectiles made developable any grains that they hit, the grains that were missed not being developable but being hit later if they continued to be exposed to the radiation. Naturally, the bigger the grains, the more likely are they to be hit, so that a calculation can be made of the relation between the size and the percentage number of grains which will become developable after a given exposure.

When this was tested experimentally, it was found that in the plates which were used in which the grains are spread out in a single thin layer, the grains tended to stick together in clumps, two or three small grains attaching to each other, and it was found experimentally that if one of these grains is affected by light, the whole clump becomes developable. The developability of a clump by infection from a single exposed grain has been questioned. Svedberg examined this subject for his own plates and found specifically that no such infection occurred. On the other hand, Trivelli and Righter measured many clumps on their plates and considered the existence of infection to be proved beyond doubt.<sup>24</sup> It is quite probable that the discrepancies are due to differences in

---

<sup>24</sup> Trivelli, A. P. H., Righter, F. L., and Sheppard, S. E., "On the Mutual Infection of Contiguous Silver Halide in Photographic Emulsions," *Phot. J.*, 46, 1922, p. 407.



the emulsion. Trivelli has found in recent work<sup>25</sup> that different preparations of an emulsion show great differences in the tendency of clumps to become infected, some preparations showing a large proportion of clumps which are entirely developable, while in other preparations it is quite possible to develop one grain of an apparent clump and to have other grains showing no development.

On any chemical theory of differences of sensitiveness in the grains, it is difficult to imagine that a clump of grains will be more sensitive than the most sensitive single grains, although we could imagine that a big grain would be more sensitive than a smaller grain, but on a light projectile theory, a clump of small grains will act just as if it were one big grain of the same area, because the chance of one of the grains being hit by a light projectile and making all of them developable is just the same as if the total area were filled by one grain. It is consequently possible to calculate the rate at which clumps containing different numbers of grains will be affected by the light, and when this was measured experimentally for clumps containing two, three, four, and more grains, it was found that the values of "sensitiveness" of the different clumps agree very well with those which were calculated on the light projectile theory as developed by Silberstein.

Whatever the projectile of light is, it must be associated in some way with waves, because, as was said earlier, the frequency of the vibration emitted is proportional to the energy of the electron which produced it, and so, while we have gone back to a projectile theory of light, instead of the idea of a continuous wave front, we have not abandoned waves. Silberstein suggests that the projectiles rather than being called "corpuscles," which gives the idea that they are round, should be called "light darts" and should be imagined to consist of a long train of waves of very small diameter travelling with the velocity of light.

Einstein has found that the emission of energy from an atom emitting its spectral radiation must be definitely oriented in direction and cannot be propagated in a spherical wave, the atom recoiling and thus preserving the thermodynamic equilibrium.

It is obvious that this theory of light darts would meet the difficulties which are offered by the phenomena of X-rays and photoelectricity to the idea of a continuous wave front, while not

---

<sup>25</sup> A letter on "The Effect of Development upon Grain Clumps," *B. J.*, 69, 1922, p. 687.



excluding the possibility of the formation of interference and diffraction effects, and at first sight it would seem to offer a solution of the problem of the integration of exposure by the silver halide grains of the emulsion, since we might assume that instead of a grain integrating energy falling upon it until it had received enough to make it developable, it was not affected at all until struck by a quantum of light and then became developable completely. If this were so, however, we should expect that the amount of energy necessary to make a grain developable would be, on the average one, and at most, a few quanta, more than one being necessary because of the chance that a fresh grain would not be struck by every "light dart" falling upon the emulsion, some falling between the grains and others striking grains which were already developable.

It has long been known that the amount of energy required to make a grain developable is in absolute amount very small, and in my paper before the Institute in 1915 it was suggested that quite possibly it was of the order of one quantum per grain, this being derived from a rough calculation by P. G. Nutting based on some measurements of the energy required to make a plate developable to a given density.

Up to the present there have been very few trustworthy measurements of the amount of energy necessary to make photographic plates developable, and the measurements available are not in such a form that a satisfactory factor for the number of developable grains after exposure can be found. Leimbach<sup>26</sup> made a number of careful measurements of the energy transmitted through a monochromatic spectrophotometer. He found that for a Schleussner plate 0.6 erg per square centimetre would give a density of unity at a wave-length of  $450\mu\mu$ . In some work which has just been started in our laboratory we are getting results of the same order as those of Leimbach, and I think we may conclude as a preliminary statement that for high-speed emulsions several hundred quanta of violet light are necessary per grain in order to make the grain developable.

If this result is confirmed, the light dart hypothesis would scarcely seem to be sufficient by itself to explain the integration of energy by the emulsion, and we are thrown back on to the idea of differential sensitiveness among the grains or of spots of

---

<sup>26</sup> *Zeit. Wiss. Phot.*, Vol. 7, No. 5, pp. 157 and 181; *Sci. Abs.*, Vol. 12, p. 1209.



limited area on the grains, so that of the hundreds of quanta striking a grain only one may be considered to be operative, the rest falling upon the insensitive portions of the grain. Suppose that the fraction of a grain which is sensitive is  $\varepsilon$  and this consists on an average of  $\overline{K}$  spots of  $\omega$  area; then,

$$\overline{K} \omega = \varepsilon a.$$

Now, if a grain has no spots it will be quite insensitive and will not be developable no matter how long it is exposed, so that the value of  $\overline{K}$  and  $\omega$  can be determined experimentally by counting the grains left over after a very prolonged exposure.

The distribution of sensitiveness among the grains of an emulsion may thus be ascribed to (1) a heterogeneity in the radiation, together with a variation of sensitiveness either over the whole surface or in the form of local centres in the material, in which case the sensitiveness will be a probability function of the size of the grain, or (2) a distribution of centres of sensitiveness, which will also be distributed according to a probability function. This function may either be proportional to the volume or to the area of the grain, while the chance of being hit by a light dart would be proportional to the area only. It seems to be possible that no crucial distinction between the two hypotheses can be made by direct photographic determinations. A study, however, of the effect of desensitizers upon the developability of grains exposed to light may make a decision possible. In any case, a question of great importance in connection with the latent image is the amount of energy required to make the silver halide developable. If the new determinations show that several hundred quanta of violet light per grain are necessary, then a revision of ideas relating to the latent image itself will follow as compared with those ideas derived from the belief that the energy available is only one quantum per grain, in which case it is clear that the latent image must depend upon a change occurring in a single atom of silver or halogen, since the only work we can imagine one quantum capable of doing to be the release of a single electron from an atom. If several hundred quanta per grain are available, then it is clear that not one atom of silver per grain may be affected but that several hundred atoms may be changed and that an appreciable, though very small, amount of chemical decomposition may be effected by the energy available. More important



still, quantitative differences in the amount of latent image present in a grain become possible. If only one quantum per grain is available, a grain is either exposed or not exposed, but if energy corresponding to an amount of several hundred quanta are used, we might imagine that a grain could become partly exposed, so that, for instance, it might be developable by a developer of high reduction potential but not by one of low reduction potential. Moreover, grains might clearly be of different degrees of sensitiveness, that is, they might require different amounts of energy to make them developable, and the whole idea of quantitative differences in sensitiveness and exposure, which is so difficult if we imagine one quantum of energy per grain to be sufficient to produce a complete change in the grain which will make it developable, becomes perfectly intelligible. On the other hand, the division of the sensitive area into a number of small sensitive spots, which accords with the ideas both of Silberstein and of those other workers such as Svedberg who have located sensitiveness in "centres," would still enable us to retain the idea that a single quantum of energy is sufficient for exposure if it reaches one sensitive spot.

In concluding this paper I feel that my presentation of the subject demands some apology. I have endeavored to summarize the recent work done by a number of workers on the theory of photographic sensitiveness, but I have not been able to present a clear and definite creed drawn from their findings. The facts which have been ascertained are not as yet sufficiently coördinated to enable us to distinguish between the several explanations which are possible and I have chosen rather to put forward, as fairly as I can, the views held by others, than to select one specific theory and advocate its adoption. The work of the next few years will undoubtedly clear up much that is dark and uncertain at the present time.

---

**Spontaneous Decomposition of Ammonium Chlorate.**—According to FRED FAIRBROTHER, of Victoria University, Manchester, England (*Jour. Amer. Chem. Soc.*, 1922, xlv, 2419-2422), the rate of the spontaneous decomposition of ammonium chlorate is autocatalytically accelerated when the products of the decomposition are not quickly removed. The solid mass, which remains at the end of the reaction, is almost pure ammonium nitrate, and is free from chlorides.

J. S. H.



**The Relation between the Evolution of Heat and the Supply of Energy during the Passage of an Electric Discharge through Hydrogen.** J. KEITH ROBERTS. (*Proc. Roy. Soc., A* 714.)—"In this paper an account is given of measurements of the heat evolved by the passage of a known current under a known potential through a hydrogen discharge tube. The experiment was suggested by Sir Ernest Rutherford as a possible test of the hypothesis in which he supposed that a much closer combination between an electron and a hydrogen nucleus than that existing in the hydrogen atom might occur under suitable conditions. The experiments of Aston, which show that the masses of all atoms except hydrogen are whole numbers, indicate that the close binding of electrons and positive nuclei causes a decrease of mass, owing to the interaction of the fields. Such a decrease of mass might be expected to occur if the supposed close combination of a single hydrogen nucleus and an electron took place. We should expect this decrease of mass to be accompanied by an evolution of energy, since a mass  $m$  has energy  $\frac{1}{2} mc^2$  associated with it,  $c$  being the velocity of light."

The hydrogen discharge tube, 19 cm. long and 2.5 cm. in diameter, was placed in oil, the calorimetric liquid, contained in a Dewar flask. When the discharge traversed the tube the temperature of the oil rose. This was measured by four thermo-junctions in the liquid. Immersed in the same oil was a heating coil. Through this current was passed until the same elevation of oil temperature was attained as had been produced by the operation of the hydrogen tube. Then the two quantities of electrical energy which had caused the same rise of temperature were compared. These agreed to about .3 per cent. for a series of experiments. This shows that "the conservation of energy holds in the energy changes in a discharge tube."

An interesting by-product of calculations in this paper is this, that after an electron has fallen through one volt its energy of translation is equal to that of a gas molecule at  $7730^\circ$  abs. Under the operating conditions of the tube an electron fell through as much as 330 volts. This would correspond to a temperature of  $2,600,000^\circ$  abs. This is of the same order of magnitude as the temperature held by Eddington to obtain in certain types of stars. "In order to account for the fact that the energy radiated by giant stars is too great to be supplied by the loss of gravitational potential energy by contraction, it has been suggested that atomic changes of this nature occur in these stars. If 1 per cent. of the mass of a giant star were converted from hydrogen to helium the energy evolved would be sufficient to supply the star with energy for  $1.5 \times 10^7$  years." Two hundred ergs per second would be radiated by the mass of the star. Applying this rate to the very small mass of hydrogen in the experimental tube it was found that any effect that might be expected from this radiation was too small to be detected. The hypothesis advanced by Eddington as to the origin of stellar radiation is therefore not affected by the results of this experiment.

G. F. S.



# THE TRANSFORMATION OF COLOR MIXTURE EQUATIONS FROM ONE SYSTEM TO ANOTHER. II. GRAPHICAL AIDS.\*

BY  
HERBERT E. IVES, Ph.D.,

Member of the Institute.

## INTRODUCTION.

IN a previous paper under this title<sup>1</sup> I have outlined the processes necessary for transforming color measurements from one trichromatic system to another, and from a trichromatic to the monochromatic system (spectral hue, luminosity and purity). In the present paper the same problems are considered, but the solutions are worked out in graphical instead of algebraic form. This form of treatment is made possible by consenting, at least during part of the work, to a limitation in the generality of the problems to be handled. This limitation is that the absolute luminosity, or the level in the space figure representing the color system, is not considered. We shall be here concerned primarily when dealing with the two systems of color measurement with the *relative* amounts of our trichromatic primaries and with the *relative* amounts (on a luminosity scale) of spectral color and white.

This limitation of the problems is one which is ordinarily tacitly made in the color measurement of illuminants, for which in fact the principal calculations of the present paper were originally made. With illuminants the luminous values (*e.g.*, candle powers) may be anywhere on a scale of theoretically infinite length, not interrelated in any way with the chromatic character of the light. Luminous values of light sources are customarily the subject of separate determination, and the color measurement normally consists merely of those relative amounts of primaries or of spectral color and white to which we are here initially to be restricted. This case is to be distinguished from that of the color measurement of a transmitting or reflecting medium in which it is usual to measure the luminosity as a fraction, definitely restricted to values between zero (black) and unity (white or complete

---

\* Communicated by the Author.

<sup>1</sup> JOUR. FRANK. INST., Dec., 1915, p. 673.



transmission) whatever the value of the illumination, which latter conditions the absolute luminosity.

As the sequel shows, the limitation assumed does not narrow the range of problems amenable to graphical methods as much as the preceding paragraph would suggest. For, by the utilization of data which are accumulated in the complete processes involved, it is possible to solve certain problems in which luminosity values are an essential part. This is notably the case in the measurement of transmitting or reflecting media, for which the graphical methods become in fact very time-saving mechanical aids to performing the calculations outlined in the earlier paper.

The theory of the operations performed in the present paper is all set forth either explicitly, or implicitly, by the treatment of closely similar problems, in the previous paper. Consequently it is considered permissible here to present several specific problems practically as *worked examples*, with a minimum of explanation.

#### DATA REQUIRED FOR THE SOLUTION OF THE PROBLEMS.

The experimental data necessary to the complete quantitative solution of the problems to be considered are as follows:

1. The amounts of a reference or standard set of trichromatic primaries which must be mixed to reproduce a spectrum of known energy distribution; the plot of these through the spectrum will be referred to as "spectral mixture curves."

2. The distribution of luminosity through a spectrum of known energy distribution.

3. The distribution of energy through the spectrum corresponding to white light.

4. The distribution of energy through the spectrum of the trichromatic primaries which are to be used in making the measurements. These primaries will be referred to as the "working primaries."

For the first of these we shall use the Koenig "fundamental sensation" curves, modified in the manner dictated by consideration of the luminous values of the sensations, as developed in the previous paper. These are shown in Fig. 1 (light lines, arbitrary scale) plotted for an equal energy spectrum, on the basis of equal areas of the red, green and blue curves for a "white light" defined as black body radiation corresponding to  $5000^{\circ}$  absolute. In Fig. 2 they are shown as plotted for white light so defined, Tables I and II give the numerical values used.



For the distribution of luminosity we shall use the equal energy spectrum luminosity curve or luminous efficiency curve obtained by the present writer and published as an element of "The Photometric Scale."<sup>2</sup> It is also shown in Fig. 1 (heavy line, maximum value unity) and Table I, column 2. This differs slightly from the curve used in the earlier paper.

For the distribution of energy in white light we shall use, as in the earlier paper, the emission curve of a black body at 5000°<sup>3</sup>

TABLE I.

TABLE II.

Equal Energy Spectrum.					White Light Spectrum.				
$\lambda$	$\lambda$	RS	GS	BS	5000° BB	$\frac{L}{\lambda \times BB}$ 5000°	RS	GS	BS
.38 $\mu$		0.0		0.0	.610		0.0		0.0
.39		.0045		.0757	.641		.0029		.0485
.40	.0024	.0107		.186	.684	.0016	.0073		.127
.41	.0032	.0163		.319	.722	.0023	.0118		.230
.42	.0096	.0190		.482	.758	.0073	.0444		.365
.43	.018	.0148	0.0	.743	.791	.0142	.0117	0.0	.588
.44	.029	.0079	.0048	.929	.821	.0238	.0065	.0039	.763
.45	.041	0.0	.0174	.949	.846	.0347	0.0	.0147	.803
.46	.058	.0010	.0380	.867	.872	.0506	.0009	.0319	.756
.47	.090	.0101	.0670	.705	.893	.0804	.0090	.0598	.630
.48	.138	.0222	.109	.461	.914	.126	.0203	.100	.421
.49	.215	.0617	.165	.233	.932	.200	.0575	.154	.217
.50	.341	.123	.244	.123	.948	.323	.117	.231	.117
.51	.493	.199	.346	.0807	.964	.475	.192	.334	.0778
.52	.638	.275	.453	.0534	.976	.623	.268	.442	.0521
.53	.795	.340	.525	.0366	.986	.784	.335	.518	.0361
.54	.919	.399	.569	.0285	.991	.911	.396	.564	.0282
.55	.992	.441	.577	.0216	.998	.990	.440	.576	.0216
.56	.999	.466	.554	.0167	1.001	1.00	.466	.555	.0168
.57	.953	.470	.494	.0137	1.004	.957	.472	.496	.0138
.58	.879	.462	.394	.0105	1.004	.883	.464	.396	.0105
.59	.777	.438	.287	.0051	1.004	.780	.440	.288	.0051
.60	.633	.398	.198	.0024	1.003	.635	.399	.199	.0024
.61	.491	.348	.133	.0009	1.002	.492	.349	.133	.0009
.62	.362	.289	.0923	.0005	.997	.361	.288	.0921	.0005
.63	.240	.214	.0555	.0002	.992	.238	.212	.0551	.0002
.64	.164	.153	.0340	0.0	.983	.161	.150	.0334	0.0
.65	.101	.0957	.0184		.970	.0936	.0934	.0180	
.66	.060	.0580	.0100		.967	.058	.0561	.0097	
.67	.038	.0344	.0054		.959	.0364	.0380	.0052	
.68	.022	.0148	.0023		.949	.0209	.0140	.0022	
.69	.013	.0096	.0014		.939	.0122	.0090	.0013	
.70	.007	.0052	.0007		.928	.0077	.0048	.0007	

absolute. This is computed from the Wien-Planck equation using the value 14,350 for the constant  $c_2$ , and is also shown in Fig. 1, plotted to an arbitrary scale of ordinates;<sup>3</sup> the numerical values are in Table II, column 1. The luminosity curve of the white light spectrum is the product of the luminous efficiency curve by the energy distribution as shown in Table II, column 2.

<sup>2</sup> JOUR. FRANK. INST., August, 1919, p. 217.

<sup>3</sup> This value of  $c_2$  was used because the calibration of a "color temperature" standard lamp from the Bureau of Standards used in the work for which these methods were developed, was on this basis.



For the energy distribution of the working primaries we shall take the transmissions of three special colored glasses, a yellow, a green and a blue, as used in conjunction with a black body at a temperature of  $2848^{\circ}$  absolute. These primaries are used here because their characteristics have been measured in connection with another problem and are available. Any other set of three colors, well separated in the spectrum, would do as well for our present purpose. The energy distributions of these working primaries are shown in Fig. 3, the ordinates being on an entirely arbitrary scale.

**PROBLEM 1. TRANSFORMATION OF WORKING PRIMARY MIXING QUANTITIES TO REFERENCE PRIMARY MIXING QUANTITIES.**

The first step is to find the reference primary values of the working primaries. This is done by integrating the products  $E_{\lambda}, S_{\lambda}, d\lambda$  for all three working primaries, where  $E_{\lambda}$  is the energy value for a given working primary,  $S_{\lambda}$  the mixing amount of the reference primary for the reference equal energy spectrum at the wave-length  $\lambda$ . This is done graphically, taking the products of the curves of Fig. 3 and Fig. 1, and obtaining the areas of the resultant curves by means of a planimeter. The results of this operation on our chosen primaries are listed in the table below. (The units are of course entirely arbitrary.) For purposes of economy of words the reference primaries will hereafter be spoken of as "sensations," it being understood that the term is correctly applied only to the fundamental primaries which are here used.

TABLE III.

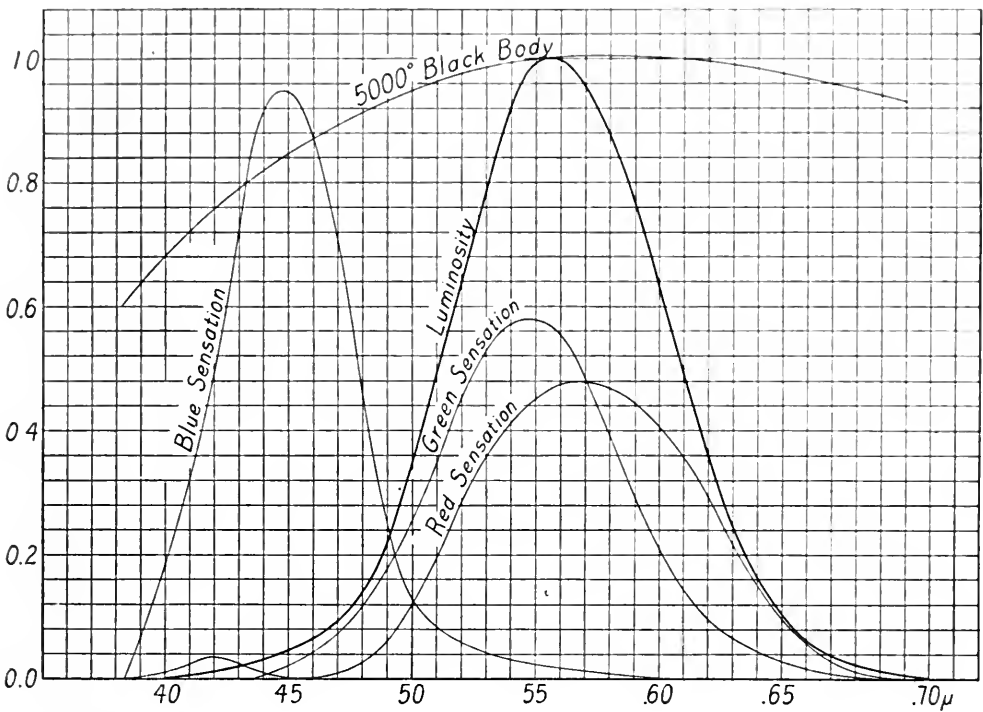
Working Primary.	Red Sensation.	Green Sensation.	Blue Sensation.
Yellow .....	.543	.352	.0114
Green .....	.372	.574	.418
Blue .....	.426	.494	.979

The sensation values are the coördinates of the working primaries in the rectangular coördinate system in which the three sensations are plotted along the axes, the scale being that for which white light is given by equal quantities of the three sensations. In Fig. 4 the triangle of which the working primaries ( $Y_1, G_1, B_1$ ) are the vertices is shown in this rectangular coördinate system. We shall call it the "working primary triangle." The straight lines joining these working primary points with the origin of coördinates, and extended, constitute loci of the same



relative proportions of the sensations, or lines of the same hue.<sup>4</sup> These may be produced to cut the plane in which lie all the points for which the sum of the sensation values is unity, on which plane the three coördinate planes mark out the fundamental reference color triangle. We shall call this the “unit-sensation-sum triangle.” In order to find where the working primary hues lie in this triangle, it is only necessary to multiply the figures in

FIG. 1.



Fundamental data required for solution of the problems considered: Heavy line; luminosity curve of equal energy spectrum. Lower set of three curves; the fundamental sensations in an equal energy spectrum. Upper curve; energy distribution through the visible spectrum of a black body at 5000° abs. here used as the standard white light.

Table I by such values as shall make the sensation sums unity for each working primary. The figures obtained are as follows:

TABLE IV.

Working Primaries.	Red Sensation.	Green Sensation.	Blue Sensation.
Yellow .....	.599	.3884	.0126
Green .....	.273	.421	.306
Blue .....	.225	.260	.515

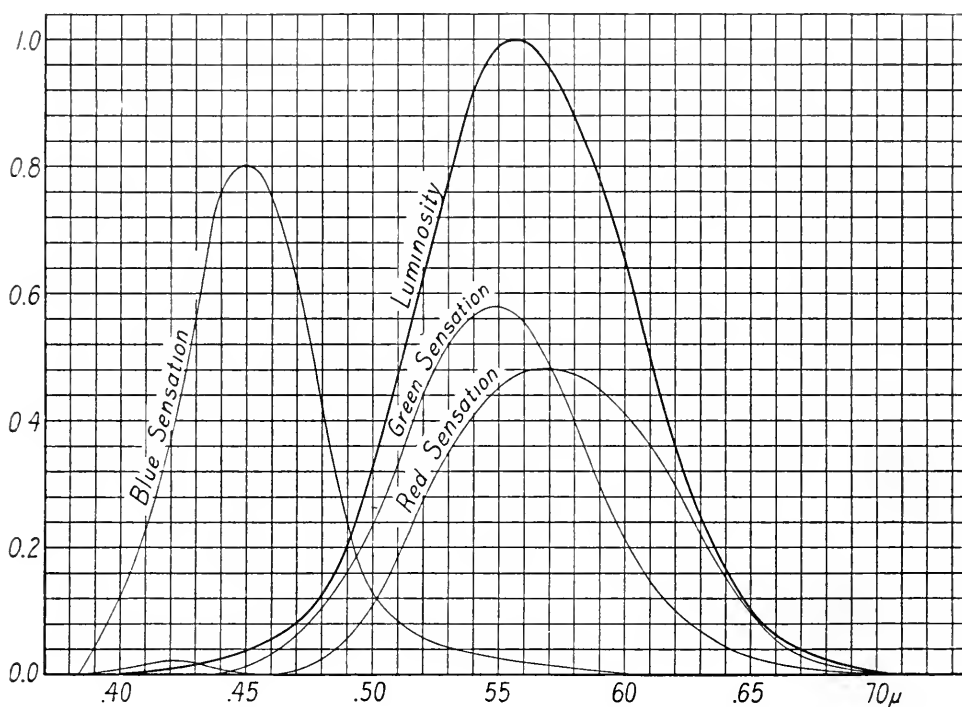
<sup>4</sup>The term “hue” is used in conformity with the practice followed in the first paper. The practice of the majority of color terminologists indicates that the term “chroma” would be preferable to designate the straight lines in question, using the term “hue” to designate the planes through these lines and the white-black line.



These sensation values are the coördinates of the vertices of a triangle lying on the unit-sensation-sum triangle, as shown diagrammatically in Fig. 4 ( $Y_2, G_2, B_2$ ). We shall call this the "working primary hue triangle."

Our problem is now to establish a one-to-one correspondence between points in the working primary triangle and the working primary hue triangle. This is a simple problem in projective geometry. If we call the coördinates of the yellow working primary  $x_1, y_1, z_1$ , and that of the blue working primary,  $x_2, y_2, z_2$ ,

FIG. 2.



Data shown in Fig. 1 as applied to white light (5000° black body).

etc., the sides of the triangle whose vertices are the origin of coördinates and these two working primaries, are of lengths,

$$\text{origin to } Y_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$$

$$\text{origin to } G_1 = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

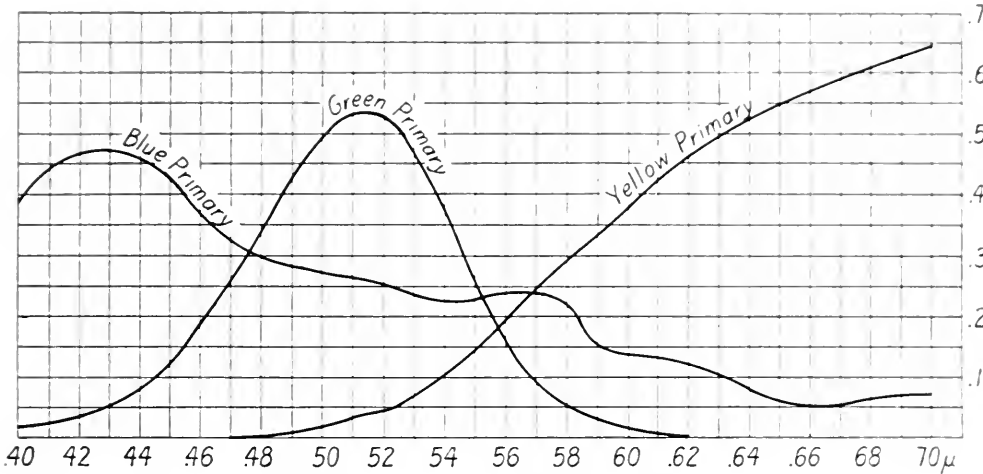
$$Y_1 \text{ to } G_1 = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

Similarly we can get the three sides of the triangle whose vertices are the origin of coördinates, the yellow and the blue vertices of the working primary hue triangle. These two triangles are shown in Fig. 5. Now we shall assume (as the only reasonable scale to work with) that the sides of the working primary triangle are



divided into equal parts. Dividing the  $Y_1 - B_1$  side of the working primary triangle, as shown in Fig. 5, into equal parts, we obtain at once the corresponding divisions on the working primary hue triangle by producing straight lines from the origin through the dividing points as shown. Upon performing the same operation for the other two sides and joining the corresponding points in the three sides we finally obtain the triangle shown in Fig. 6;

FIG. 3.



Spectral energy distribution curves of the three working primaries.

with sides unequally divided, but lying in the fundamental reference plane—the working primary hue triangle.

This triangle is the solution of our first problem. Its manner of use is simple. Suppose a color is measured in terms of the working primaries as of value

$$Y = y$$

$$G = g$$

$$B = b$$

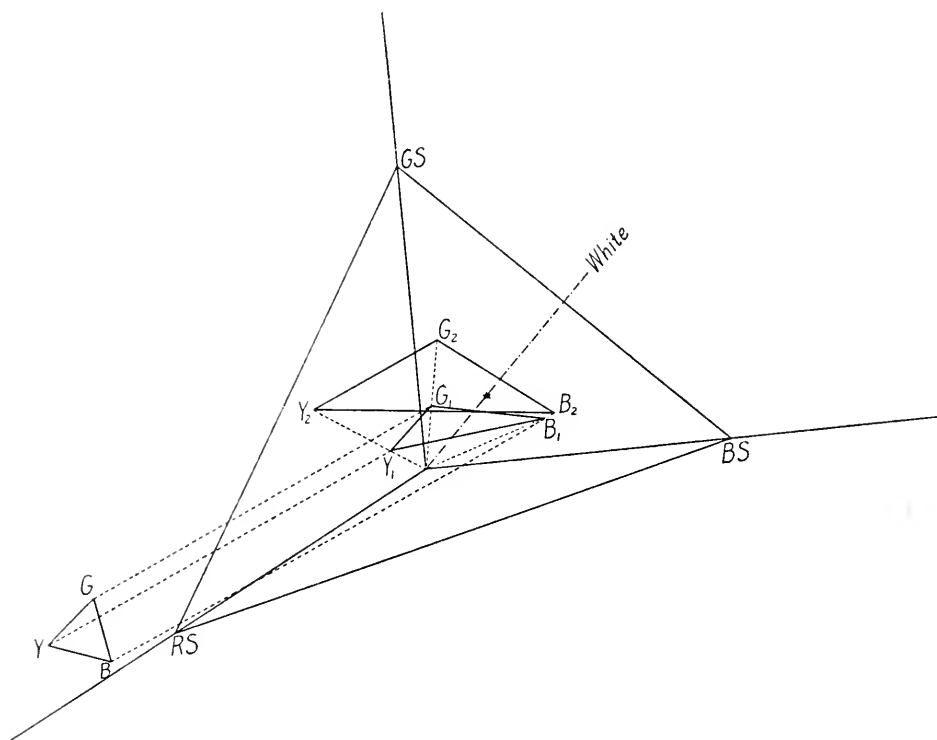
where  $y + g + b = 1$  (either as measured or by reduction). It is now only necessary to lay off a distance  $y$  units from the  $G - B$  side toward  $Y$ ,  $g$  units from the  $Y - B$  side toward  $G$ , and  $b$  units from the  $Y - G$  side toward  $B$ , in the small triangle of Fig. 6, to locate a point. The position of this point in the unit-sensation-sum triangle (on a portion of which the working primary hue triangle is superposed) gives the value of the color (or properly its hue) at once in the fundamental units. The procedure is of course reversible, the value of any color given in terms of fundamental sensation units may be transformed to working primary values. Thus the (white) centre of the fundamental triangle,



marked in Fig. 6 by a circle, is immediately read off in terms of our working primaries as  $Y = .39$ ,  $G = .25$ ,  $B = .36$ .

It may be remarked that a picture is obtained of the various projection processes involved in the transformations outlined by noting that the working primary triangle, with its sides of unequal length but each marked off in equal divisions, is the projection of an equilateral triangle of equally divided sides made by *parallel* rays on a plane at an angle to the plane of the triangle (ortho-

FIG. 4.



Diagrammatic representation of projection processes for transforming working primary values to fundamental sensation values.

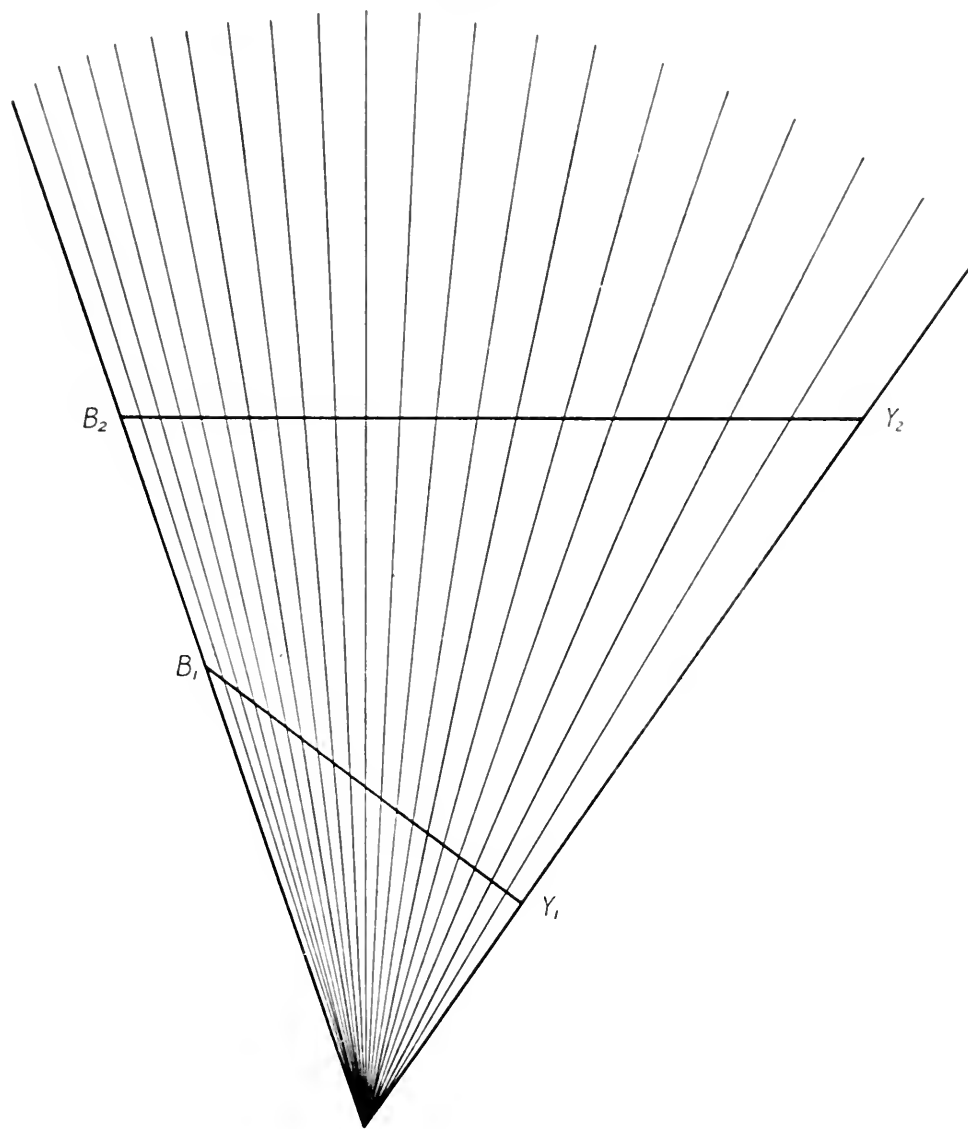
graphic projection); and that the final triangle in the unit-sensation-sum plane is the projection of the working primary triangle on that plane made by divergent rays from the origin of coördinates (stereographic projection). These projection processes are shown diagrammatically in Fig. 4.

At this point it is well to call attention once more to the limitations of the solution we have obtained. It tells us merely the location of the *hue*, that is the *relative* proportions of the three sensation primaries in the color originally measured in terms of the working primaries. This as previously noted is a limitation inherent in the graphical method. It is, however, all the infor-



mation we ordinarily need when measuring illuminants. Where absolute values in the sensation space figure are wanted, they can be arrived at by algebraic methods, provided the coördinates of some common point are known in the two trichromatic systems. In the earlier paper the common point chosen was a reference

FIG. 5.



Process for finding the scale in the unit-sensation-sum plane corresponding to equal divisions in the working primary plane.

white, and the scales used were such that both sets of measurements evaluated this white as equal admixtures of the three primaries. The same algebraic method is applicable to the present more general problem in which are handled the energy distributions of the primaries as used, irrespective of the color corre-

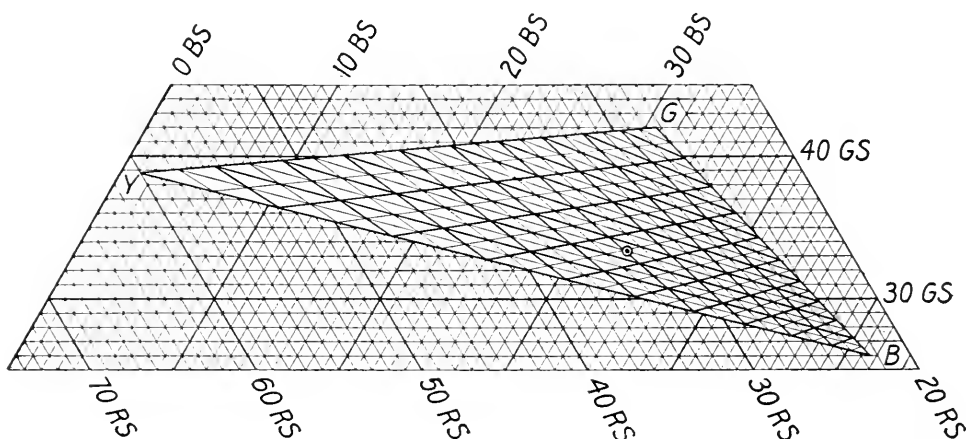


sponding to any particular scale reading. The algebraic methods necessary for this case as given in the earlier paper are adequate and probably simpler than any graphical solution, since the latter would involve three dimensions.

**PROBLEM II. DERIVATION OF MIXTURE CURVES OF THE SPECTRUM.**

The kind of diagram developed in Fig. 6 may be utilized in a problem met in the construction and use of trichromatic colorimeters. This problem is the determination of the *mixture curves of the spectrum* for the spectrum patches or colored glasses used as the instrument's working primaries. It is a problem which occurs also in the application of the three-color principle to color

FIG. 6.



The working primary triangle transferred to the equal-sensation-sum plane.

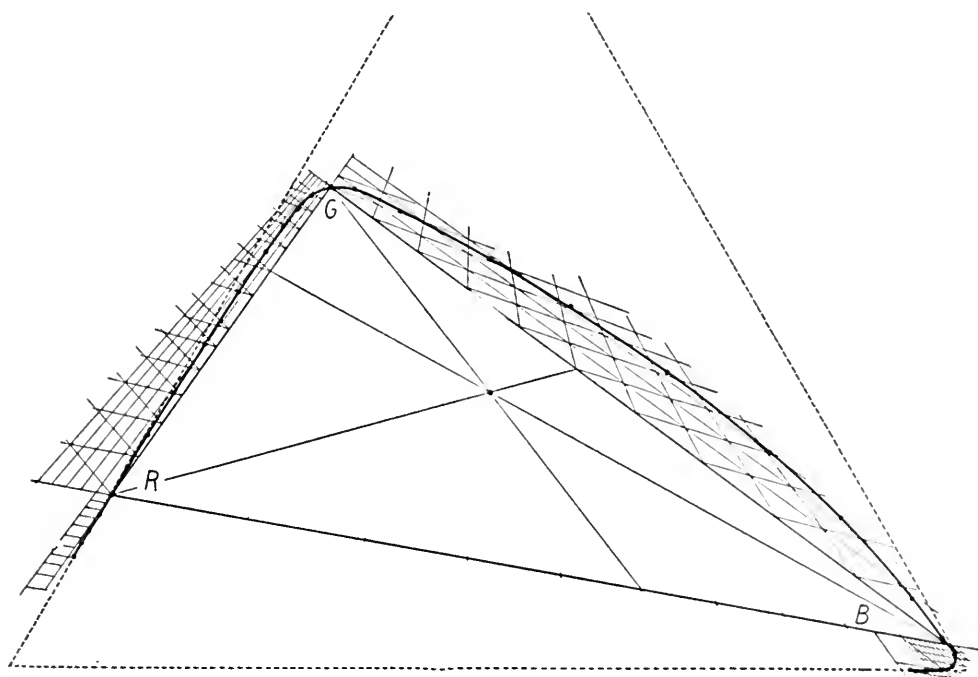
photography, where the "taking" screen transmissions must conform (assuming uniform photographic action through the spectrum) as closely as possible to the spectral mixture curves of the colors corresponding to the "viewing" screens, thus necessitating a knowledge of the latter curves.

The initial steps in this problem are identical with those set forth in the earlier paper and in the preceding sections of this. We first find by determining their sensation values what amounts of the instrument's primary colors mix to give white; the energy distributions of these primaries in the proportions used constitute the "working primaries." Their relative mixing proportions to yield all the colors in the sensation triangle are determined by constructing a diagram similar to Fig. 6. (Where a large range of colors is to be measured or reproduced the instrument primary



triangle will be relatively much larger and lie closer to the spectrum than does the inner triangle of this figure.) From this the *percentage mixture curves* of the spectrum may be read off at once, that is, the relative amounts of the three primaries, on a scale of maximum value unity, necessary to match the spectral hue at each wave-length. This is as far as the graphical method takes us. The next step is to obtain from these percentage curves the ordinary spectral mixture curves. In these latter the three elements are of the *shapes* which add to give the luminosity curve

FIG. 7.



Projection of Maxwell primary working primary triangle on the modified Koenig sensation triangle.

of the spectrum, when the amount of each primary is represented in its luminosity value, but of the *size* dictated by the convention that the areas under the three elementary curves shall be equal for white light.

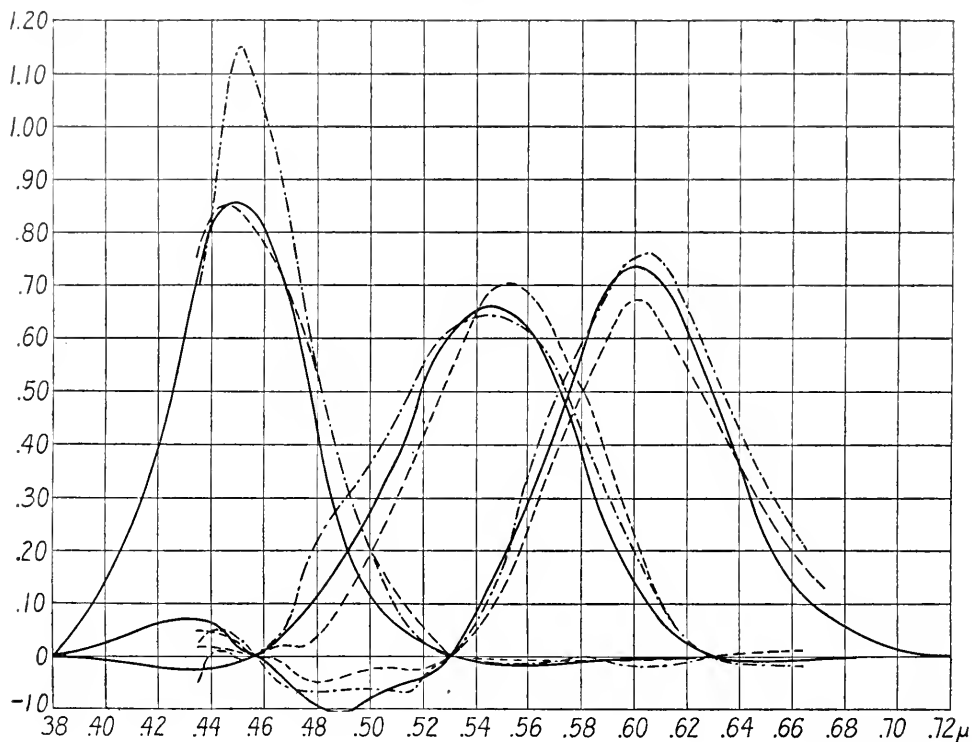
In order to solve this step of the problem one method would be to utilize the luminosity curve of the (white light) spectrum, and the luminous values of the primaries, as determined from their spectral composition and the equal energy spectrum luminosity curve (Fig. 1). Then, having found, as above, the relative proportions of the three primaries needed to match any wave-length (percentage mixture curves), the rest of the problem is



the purely arithmetical one of finding the actual amounts of the three primaries, taken in these proportions, whose total luminosity shall equal that of the spectrum at the wave-length in question. These actual amounts (on a scale which is determined by the arbitrary choice of spectral patch width and other units in carrying through the work) form, when plotted, the desired mixture curve of the spectrum for the primaries chosen.

The method just outlined depends for its success on a knowl-

FIG. 8.



Spectrum mixture curves for Maxwell's primaries, as computed from modified Koenig data (full line). Maxwell's own data are shown by the dashed line, those of his assistant by the dot and dashed line.

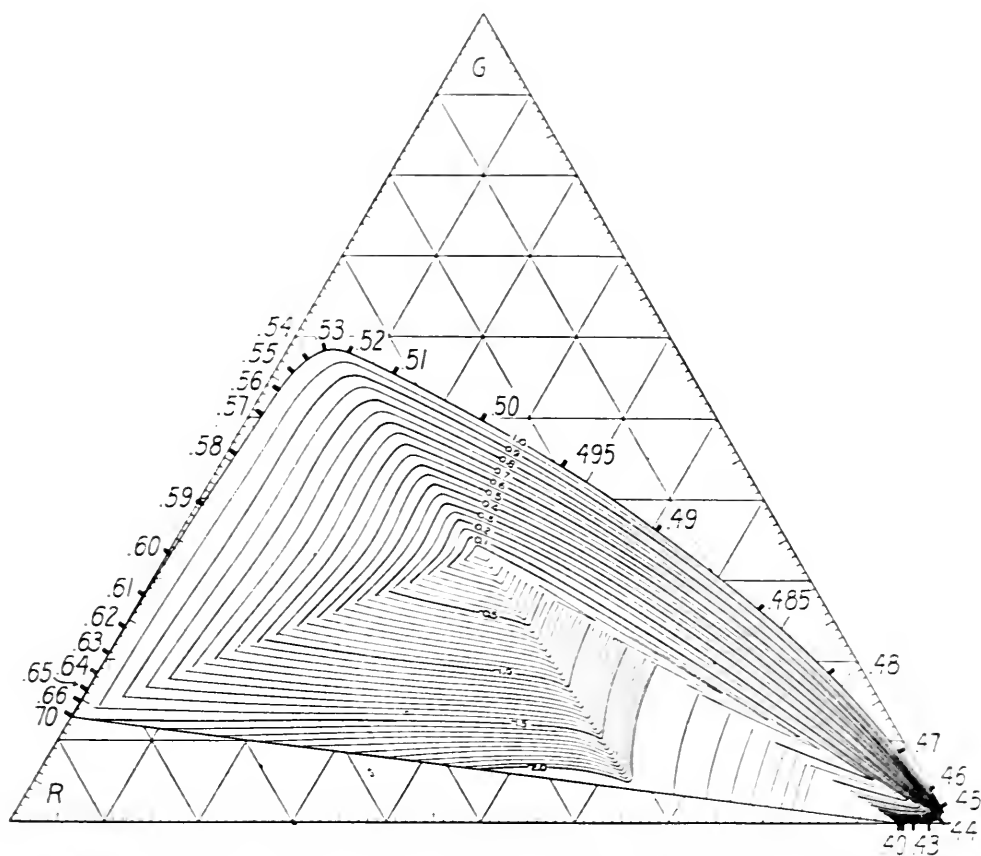
edge of the luminous values of the primaries and on the exact agreement of the three-color mixture data with the spectral luminosity curve, *i.e.*, they should be determined by the same observers and under the same conditions. An alternative means is available when the spectrum mixture curves of the fundamental primaries (*e.g.*, sensations) are known, as has been assumed. This method consists in taking at each wave-length such quantities of the working primaries in the proportions indicated by the percentage mixture curves as shall together give the amounts of the fundamental primaries present, as shown on the mixture curves of the latter.



In practice it is only necessary to assure that one of the fundamental primaries is present in proper quantity, for instance, the red through the orange and red, the green through the yellow and green, etc.

Using this latter method I have determined, as a matter of interest, the mixing proportions of the three primaries used by Maxwell in his pioneer investigation in 1859. Fig. 7 shows the

FIG. 9.



The fundamental sensation triangle, showing (outer curve) the position of the spectrum, (inner curves) the amounts of the spectral colors, on a luminosity scale, to be mixed with white to match all colors from white to spectrum.

necessary parts of the working primary triangle as projected on the sensation triangle, where the wave-length scale on the spectrum is as in Fig. 9, and Fig. 8 shows the spectrum mixture curves as computed therefrom (full lines). The dashed and dot and dashed lines are the data of Maxwell's two observers as reduced to a normal spectrum. The agreement thus shown between Maxwell's observers and the mean observer represented by Koenig's curves, as arranged and transformed in the first paper of this study, is on the whole surprisingly good.

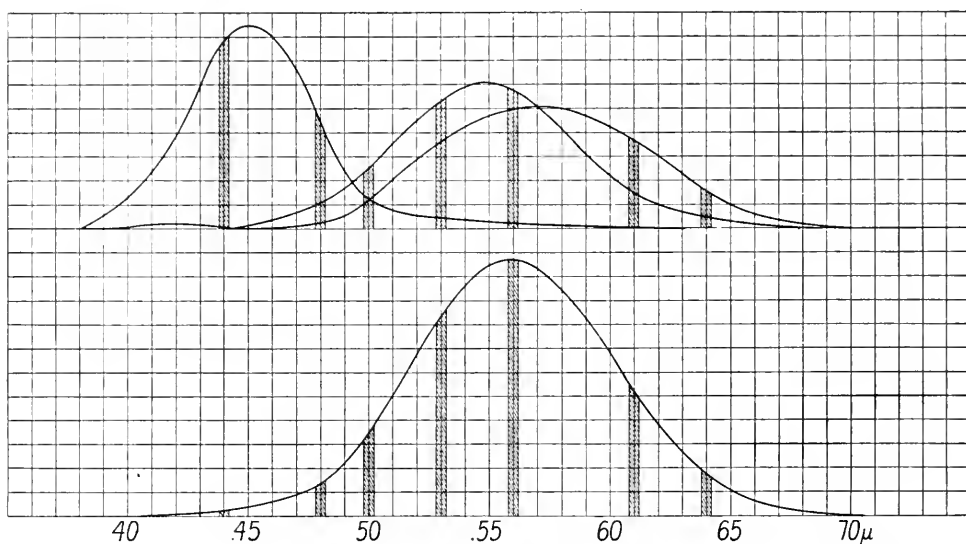


Attention may here be called to the fact that statistical studies of color vision, such as are desirable to establish an average eye for purposes of color specification, could be most simply made by determining mixture curves of the spectrum with some convenient set of three primaries, as done by Maxwell. These curves could then be transformed to any set of primaries decided upon as rational, by the transformation methods here set forth.

**PROBLEM III. TRANSFORMATION FROM TRICHROMATIC TO MONOCHROMATIC SYSTEM.**

We shall take as our trichromatic system the fundamental sensation system defined by the curves of Fig. 1. Any other tri-

FIG. 10.



Luminosity curve and sensation curves for white light (5000° black body), divided into strips for transformation process from trichromatic to monochromatic system.

chromatic system defined by a set of spectrum mixture curves could be used equally well. The spectrum in the fundamental sensation system is represented in the unit-sensation-sum triangle by the curve, marked in wave-lengths, of Fig. 9.

The first step is to plot to the same wave-length scale both the luminosity distribution, and the sensation distribution for white light, the data for which occur in Table II, columns 2, 3, 4 and 5, and in Fig. 2. The resultant curves are shown in Fig. 10 (arbitrary scales). Next we divide the spectrum into a large number of narrow strips of equal width, of which several are shown in the figure, the width being small enough so that each is substantially monochromatic. In the present case the strip width chosen was



.004 $\mu$ . The third step is to find the sensation values of each strip, in terms of the sensation values for the integral spectrum, that is, the area in the strip under each of the three sensation curves, referred to the total area under the corresponding curve taken as 1/3. To illustrate, in the strip .478 $\mu$  to .482 $\mu$  the sensation curve areas included are, in terms of the sum of the total white light sensation as unity,

$$RS = .00059 \quad GS = .0026 \quad BS = .0106$$

In the rectangular coördinate system in which white light corresponds to equal sensations, these spectral strips form a series of points lying along a closed curve very close to the origin of coördinates ( $C_1$ , Fig. 11).

It is now our purpose to find the coördinates of spectral colors which shall be *equally luminous with the integral white* of the unit-sensation-sum triangle. In order to do this we first determine the areas of the monochromatic strips in the luminosity curve diagram, in terms of the total luminosity of the white. These determined, we multiply the sensation coördinates just obtained by the reciprocals of these relative luminous values. We thus obtain a second spectral curve in the space diagram all points of which correspond to equally luminous spectral strips, each of the luminosity of the integral white ( $C_2$ , Fig. 11).

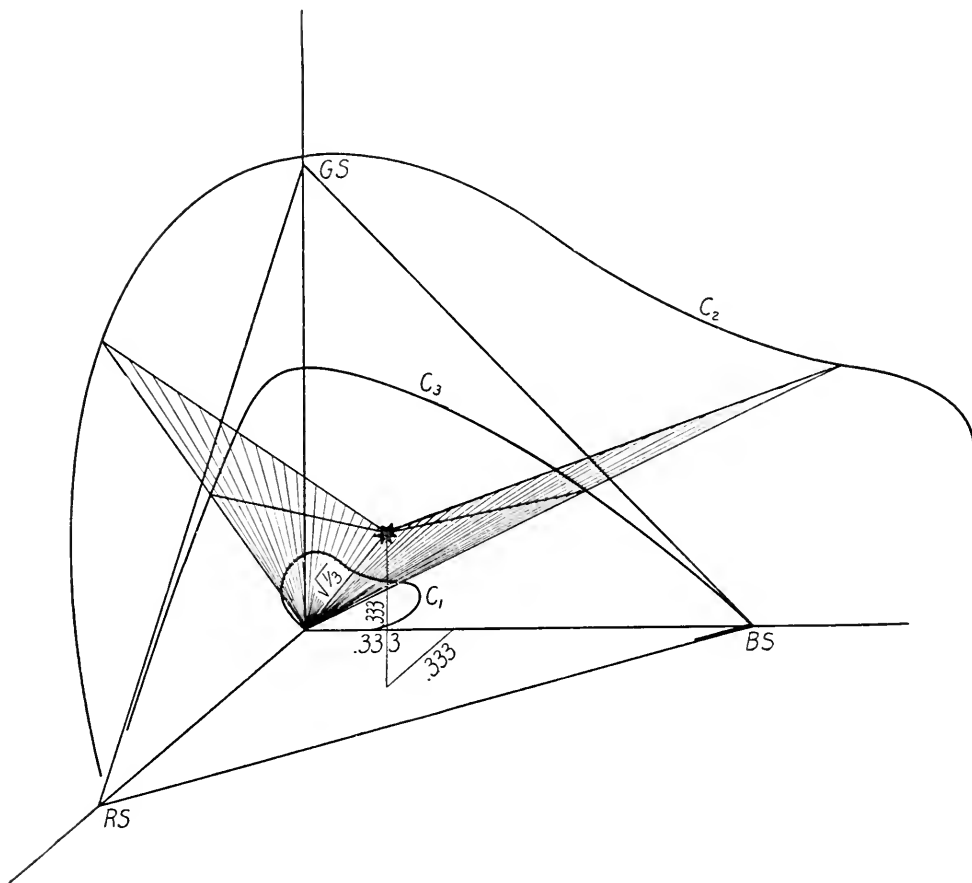
From this point the procedure is identical with that outlined in the last section. We find the distances from each of these equally luminous spectral points to the origin and to the white centre of the unit-sensation-sum triangle (distant  $\sqrt{\frac{1}{3}}$  from the origin of coördinates). The positions of the spectral strips in the unit-sensation-sum triangle are derived in the way already described, from which their distances to the origin of coördinates and the white centre are fixed. These positions form a curve which is the one shown in Fig. 9, marked with wave-lengths. We then have for each strip two triangles with the same vertex and vertex angle, the base of one of which lies in the unit-sensation-sum plane, while the base of the other connects the white point in that plane with the equally luminous spectral color. This latter base line we divide into equal parts, and join the dividing points to the origin by straight lines. The points where these lines cut the plane of the unit-sensation-sum triangle are the dividing-points on the



line in that plane connecting the white point with the hue of the spectral strip, corresponding to our equally spaced scale between equally luminous white and spectral color. The whole process is shown diagrammatically in Fig. 11.

It is now only necessary to perform this operation for a sufficient number of wave-lengths to cover the spectrum, after which the resultant points are to be joined up into curves as shown in

FIG. 11.



Diagrammatic representation of the projection processes for transforming sensation values to spectral hue and relative amounts of spectral color and white.

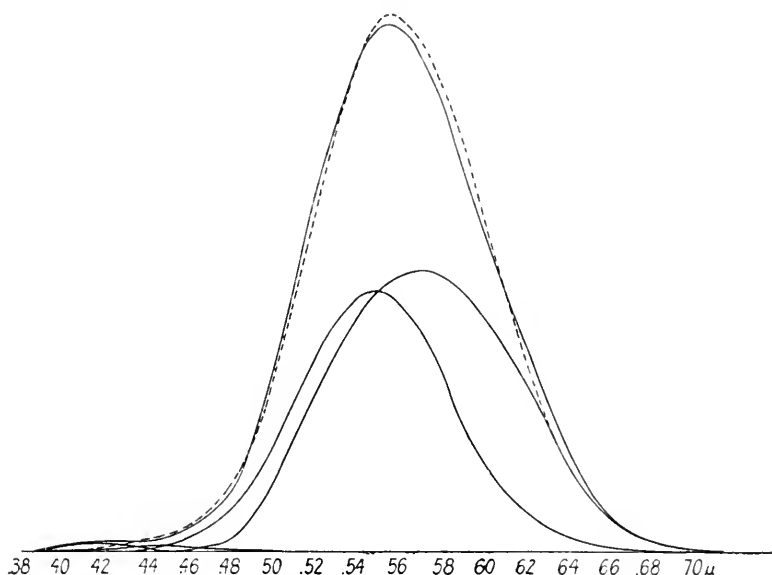
Fig. 9. In this figure any color (hue) is represented by a point; its spectral hue is obtained by producing the line joining the point and the white centre until it cuts the spectrum curve. The amount of spectral color on a luminous scale necessary to take to match the color (purity or saturation) is the length of this same line measured from the white centre and read off from the intercepting curves, which are numbered from zero (white centre) to 1.00 (spectral color). The amount of white is the difference between



this number and 1.00. For instance,  $1.00\ C = .15\lambda + .85\ W$ . For purples the scales have simply been continued to negative values. The equation of a purple is formed in the same way as for any other color, that is, so that the sum of spectral color and white shall be 1.00. For instance,  $1.00\ C = -.15\lambda + 1.15\ W$ , or  $1.00\ C + .15\lambda = 1.15\ W$ .

The background of the diagram, Fig. 9, is the fundamental sensation triangle; points on either system can be located on the other by the use of a straight edge. A convenient way to print

FIG. 12.



The three sensation curves for white light plotted according to their luminous values. Their sum is the upper full line curve; the dashed line is the luminosity curve for white light.

diagrams of this sort would be to have each set of coördinates in a different color, so that they could overlap without confusion.

Thus far the process developed is adequate only for fixing the hue of a color, that is, we have merely its spectral hue and purity in the monochromatic system, or its relative proportions of red, green and blue, on the trichromatic system. These, as earlier noted, are all of the data ordinarily required in the color measurement of illuminants. In order to make the complete transformation of measurements from one system to the other, we must know the luminosity values of the trichromatic primaries; in this case of the three fundamental sensations. We have thus far in the present treatment steered clear of assigning luminosity values to the sensations, although each monochromatic strip used in the



processes based on Fig. 10 actually gives values for one of a set of simultaneous equations from which these may be obtained. In the earlier paper luminous values for the fundamental sensations were derived by the solution of such equations. In order to fit the luminosity curve of the equal energy spectrum used in the present paper slightly different values are necessary, as follows:

Luminous value of red sensation in white light .....	.568
Luminous value of green sensation in white light .....	.426
Luminous value of blue sensation in white light .....	.066

It may be noted that the summation of the three sensation curves with their weights assigned as shown in Fig. 12 gives a check with the white light luminosity curve which is not as close as the previously derived values yielded in connection with the luminosity curve then used. In default, however, of sensation and luminosity data simultaneously obtained, which are really necessary for the solution of these problems, the above figures are the best available.<sup>5</sup>

Suppose now that we have a complete color measurement on the trichromatic system. To reduce it to the monochromatic system we derive its spectral hue and purity by the use of Fig. 9 as already described. To obtain its luminosity value, we have merely to multiply the three sensation values, which are expressed in terms of some standard white, by their appropriate luminous values, as given in the last paragraph. The sum of these luminous

---

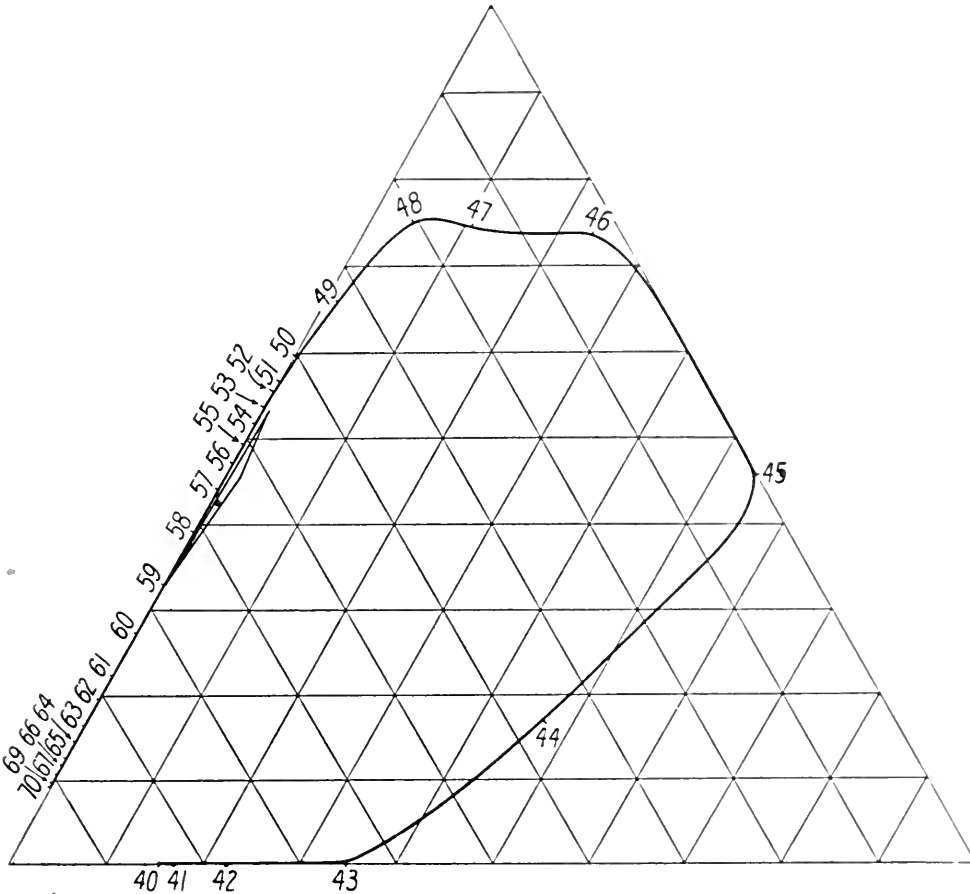
<sup>5</sup> F. Exner has recently (*Wien. Ber.*, 1921, p. 27) made a determination of the relative luminous values of the three Koenig sensation curves by an equivalent though less direct method than that used by the writer. His values are, on the unit-sum scale here used,  $R = .562$ ,  $G = .425$ ,  $B = .013$ . Exner notes the fact pointed out in the writer's 1915 paper, that no possible value can be assigned to Koenig's red curve which will permit the luminously evaluated sum to match the white light luminosity curve. Exner remedies this by arbitrarily amputating the second elevation of the red curve in the blue region of the spectrum, considering the original observations as sufficiently ill determined to warrant this. He then so modifies the remaining curves that the crossing points of the three are still in agreement with his own earlier determination. The position of the crossing points is altered by the shift in the blue primary which was the means selected by the writer to modify the Koenig curves while not conflicting with Koenig's observed values. These crossing points differ so considerably with different observers, as is shown by spectral hue discrimination data, as to make them fully as uncertain as Koenig's data. This whole matter of the exact correlation of color mixture and luminosity data offers a large field for research.



values is the desired third factor, namely, the luminosity of the color.

Conversely, if we have a complete color measurement on the monochromatic system, we obtain its relative red, green and blue proportions by the use of Fig. 9. The absolute red, green and blue sensation values are obtained by first multiplying the relative

FIG. 13.



Color triangle in the coördinate system whose units are equal luminous values of the sensations.

sensation values by their respective luminosities, and then finding the constant by which the sum of their luminosities must be multiplied to make it equal to the measured total luminosity. This constant is the figure by which the three relative sensation values must be multiplied to yield absolute sensation values.

In connection with the use of the luminous values of the reference primaries, it may well be asked why recourse is not made at once to the color mixture coördinate system in which the units are *equal luminous values* of the primaries. In such a system, points



in the color triangle (unit-sensation-sum plane) would be all of equal luminous value, and the problem of determining amounts of spectrum color and white would be one of direct measurement on a scale of equal divisions. In order to illustrate this possibility with its practical disadvantages, I have, in Fig. 13, plotted the spectrum in the color triangle form from the sensation curves as given in their luminous values in Fig. 12. It will be obvious at once that, due to the excessively low luminous value of the blue sensation, the white point, and a large portion of the colors in which we are ordinarily interested lie unworkably close to the red-green side of the triangle. Our working primary triangle, for instance, is as shown, flattened down almost to coincidence with a straight line. This makes clear that the ordinary coördinate system in which the color elements rather than luminous values are given equal rating is far preferable where color quality is the thing in question.

By means of Fig. 13 it is a simple matter to answer a question of some theoretical interest, namely, the *relative luminous values of complementaries in the spectrum*. These are found simply in this triangle by determining the relative distances of the two colors from white; their luminous values are as the reciprocals of these distances. The outstanding fact is the almost negligible luminous value of the blue light adequate to make white by mixture with yellow.

**PROBLEM IV. REDUCTION OF SPECTROPHOTOMETRIC TRANSMISSION OR REFLECTION DATA TO TRICHROMATIC OR MONOCHROMATIC SYSTEMS.**

It has been assumed in the problems thus far treated that the actual measurements are made on some form of colorimeter, that is, either by a three-color mixture instrument, or by an instrument measuring luminosity, spectral hue, and purity. An interesting case from the standpoint of *color specification* is offered where the actual measurements made are those of reflection or transmission at each wave-length, by a spectrophotometer, which are then reduced to trichromatic or monochromatic values, for simplicity of description. The advantage, other than simplicity, offered by this scheme is that the spectrophotometric values are not subject to variations due to the color vision of the observer, as are true color measurements; the original spectrophotometric data provide the full information necessary for the manufactory or standard-



izing laboratory, while the derived color sensation or hue, luminosity, and purity values provide all the information in which the user of such a commodity as a paper or paint is ordinarily interested.

The reduction of spectrophotometric reflection or transmission data to either of the color systems is performed by fairly obvious applications of the data given, and may be most easily presented in the form of *instructions*. Ordinarily the color values desired are for white light, consequently we use the data of columns 2, 3, 4 and 5, Table I, and Fig. 2.

I. *Reduction to Color Sensations*.—Multiply the transmission or reflection factor at each wave-length by the red, green and blue sensation values (Fig. 2). The areas of the resultant curves, expressed as fractions of the areas of the original curves, are the required sensation values.

II. *Reduction to Spectral Hue, Luminosity and Purity*.—Multiply the transmission or reflection factor at each wave-length by the white light spectral luminosity curve (Fig. 2). The area of the resultant curve, expressed as a fraction of the original luminosity curves gives the *luminosity*, *i.e.*, the integral visual reflection or transmission factor.

(An alternative method is to give to each sensation value, as derived under I, its luminous value. Thus if the red sensation value is multiplied by .568, the green by .426, and the blue by .006, the sum of these figures is the luminosity. Since, however, the luminosity curve is better determined than the luminous values of the sensations the method of the preceding paragraph is preferable, although it involves an extra operation.)

Next obtain the sensation values as above, multiply them by such a factor as to make their sum after multiplication, *unity*. On the unit-sensation-sum triangle (Fig. 9) locate the hue by finding the point where the red, green and blue coördinates (vertical distances from each side toward the corner corresponding to the primaries) are the three unit-sum sensations just obtained. To find the *spectral hue*, draw a line from the centre of the triangle (white) through the point, continuing it to cut the spectrum, and read off the wave-length. The *purity* (amount of spectral color in luminous units) is read off the intersected curves which are roughly concentric with the white point.



*Illustrations.*—An orange of medium saturation could have values

Luminosity .....	.43
Spectral hue .....	.601 $\mu$
Purity .....	.74

A purple would be represented by its complementary hue, and its purity by a minus value, thus:

Luminosity .....	.34
Spectral hue .....	(.50 $\mu$ )
Purity .....	-.22

#### DISCUSSION.

It need hardly be pointed out that while in each of the problems considered the numerical results are dependent on the particular trichromatic reference frames chosen, the results obtained for the reductions to hue, luminosity and purity will check with direct experiment only if the spectral mixture and luminosity curves used are consistent with each other. In the case here considered this means the consistency of the modified Koenig sensation curves with the spectral luminous efficiency curves used. It is hardly likely that the meagre data of the Koenig curves will be sufficiently in agreement with the much better determined spectral luminous efficiency curve to guarantee a close experimental check. Color measurements of illuminants made both by trichromatic and monochromatic methods, against the same standard white, would show how closely these reference curves agree, but exact data of this sort are at present lacking. The methods developed in the paper are, however, general, and applicable to more complete experimental data when available. The status of the whole problem of color measurement and specification would be materially advanced by the determination of a set of trichromatic mixture curves of the spectrum, using some well-considered set of primaries (which need not necessarily be the fundamental sensations) these curves to correspond to the same average eye and conditions of observation as does the comparatively well-determined spectral luminous efficiency curve.



## ELECTRICAL OSCILLATIONS ON LINES.\*

BY

LOUIS COHEN, Ph.D.

Consulting Engineer, Signal Corps, U.S.A.

THE subject of electrical oscillations on lines is of continuously growing importance in electrical engineering. It extends to all branches—telephony, telegraphy, power transmission, etc.—and also irrespective of the character of the electromotive force impressed direct or alternating. Whenever a change occurs in the circuit conditions, a transient effect is introduced which generally assumes the character of oscillations or wave propagations on the line. The circuit condition changes which are inevitably present in all systems are those which occur at the instant of closing or opening of the circuit.

A knowledge of what occurs on the system during the establishment of the steady state is of great importance. In the case of telegraphy, for instance, the transient effects produced by the signalling are predominant, and the speed of signalling, particularly in the case of ocean cable telegraphy, is governed and determined by these effects. In power transmission, the transient effects may at times assume a character of destructive proportions, and must be understood and carefully guarded against. The problems presented by these effects are generally complex in their nature and cannot be readily subjected to experimental investigations. Mathematical analysis must be relied upon for the study and understanding of the phenomena associated with these transient effects.

The importance of this subject was fully appreciated by engineers for some time, and many valuable papers covering different phases of the subject can be found in engineering literature. The subject, however, is so large and complex that any new presentation of it which will help to make the subject more intelligible to the engineers, throw additional light on it, and perhaps facilitate the solution of the many problems that may arise in connection with it, should prove of value. It is believed that the method developed in this paper for the solution of this class of

---

\* Communicated by General George O. Squier, Chief Signal Officer, U. S. A., and Associate Editor of this JOURNAL.



problems offers many advantages in the matter of directness and simplicity. A limited number of cases are worked out, but the method is applicable to the solution of many others. The application of the formulæ derived here to some practical problems will be considered in another paper.

Those who are acquainted with Heaviside's publications will recognize that I have made use of the expansion processes developed with such great skill by Doctor Heaviside, and have adopted them for the methods developed in this paper. I am, of course, under deep obligations to Doctor Heaviside's writings for the inspiration and suggestions derived from them.

Consider the case of a line of uniformly distributed inductance, capacity, resistance and leakage, these being designated by  $L$ ,  $C$ ,  $R$ , and  $g$ , respectively. The current voltage relations at any point on the line are expressed by the following equations:

$$\left. \begin{aligned} L \frac{dI}{dt} + RI &= - \frac{dV}{dx}, \\ C \frac{dV}{dt} + gV &= - \frac{dI}{dx}. \end{aligned} \right\} \quad (1)$$

Designate by  $p$  the time differential operator ( $p = \frac{d}{dt}$ ), and the above take the forms:

$$\left. \begin{aligned} (Lp + R) I &= - \frac{dV}{dx}, \\ (Cp + g) V &= - \frac{dI}{dx}. \end{aligned} \right\} \quad (2)$$

We may eliminate either  $I$  or  $V$  from the above equations, from which results the well-known equation of propagation:

$$\frac{d^2 V}{dx^2} = q^2 V, \quad (3)$$

where

$$q^2 = (Lp + R) (Cp + g). \quad (4)$$

The solution of equation (4) is

$$V = A \varepsilon^{qx} + B \varepsilon^{-qx}. \quad (5)$$

By the aid of the first equation of (2) we get the expression for the current:

$$I = \frac{q}{Lp + R} \left\{ -A \varepsilon^{qx} + B \varepsilon^{-qx} \right\}. \quad (6)$$

Equations (5) and (6) are the general solutions for the voltage and current, the constants  $A$  and  $B$  to be determined by the terminal conditions in each special case.



## LINE GROUNDED AT ONE END.

Assume a sinusoidal e.m.f. of frequency  $\frac{\omega}{2\pi}$ ,  $e = E\epsilon^{j\omega t}$ , impressed at one end of the line, and the other end being grounded, the terminal conditions in this case are:

$$\left. \begin{aligned} x = 0, V &= E\epsilon^{j\omega t}, \\ x = l, V &= 0. \end{aligned} \right\} \quad (7)$$

Substituting in (5), we get

$$\left. \begin{aligned} A + B &= E\epsilon^{j\omega t}, \\ A\epsilon^{ql} + B\epsilon^{-ql} &= 0. \end{aligned} \right\} \quad (8)$$

From these two equations the two constants  $A$  and  $B$  are determined:

$$\left. \begin{aligned} A &= \frac{-E\epsilon^{-ql}\epsilon^{j\omega t}}{\epsilon^{ql} - \epsilon^{-ql}} \\ B &= \frac{E\epsilon^{ql}\epsilon^{j\omega t}}{\epsilon^{ql} - \epsilon^{-ql}} \end{aligned} \right\} \quad (9)$$

Substituting in (5) the resulting equation for the potential at any point on the line at distance  $X$  is:

$$V = E \frac{\text{Sinh } q(l-x)}{\text{Sinh } ql} \epsilon^{j\omega t}. \quad (10)$$

In the above expression  $q$  includes the time differential operator which is so far indeterminate. For the steady state in the case of a sinusoidal e.m.f., the problem is very simple; operating by  $p$  on  $\epsilon^{j\omega t}$  gives  $j\omega\epsilon^{j\omega t}$ . The complete solution, however, to include the transient as well as the steady state, for either an alternating or a direct impressed e.m.f., the problem offers some difficulties. In the following a new method is proposed for the solution of this problem, which is believed to be novel and applicable to many other problems of this class. We may write equation (10) in the following form:

$$V = \frac{\text{Sinh } q(l-x)}{ql} \cdot \frac{ql}{\text{Sinh } ql} E\epsilon^{j\omega t} \quad (11)$$

By trigonometry

$$\frac{ql}{\text{Sinh } ql} = 1 - 2q^2l^2 \left\{ \frac{1}{\pi^2 + q^2l^2} - \frac{1}{(2\pi)^2 + q^2l^2} + \frac{1}{(3\pi)^2 + q^2l^2} - \dots \right\} \quad (12)$$

where

$$q^2l^2 = l^2(LP + R) \quad (Cp + g) = l^2LC \left\{ p^2 + p \left( \frac{R}{L} + \frac{g}{C} \right) + \frac{Rg}{LC} \right\}.$$



Put for brevity

$$v^2 = \frac{1}{LC}, \quad \frac{R}{L} = 2a, \quad \frac{g}{C} = 2b, \quad (13)$$

we get

$$q^2 l^2 = \frac{l^2}{v^2} \left\{ p^2 + 2(a+b)p + 4ab \right\} \quad (14)$$

and

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2} \frac{1}{p^2 + 2(a+b)p + 4ab + \frac{\pi^2 v^2}{l^2}}. \quad (15)$$

The denominator in equation (15) may be put in the following form:

$$p^2 + 2(a+b)p + 4ab + \frac{\pi^2 v^2}{l^2} = (p - k_1)(p - k_1'), \quad (16)$$

where

$$\begin{aligned} k_1 &= -(a+b) + \sqrt{(a-b)^2 - \frac{\pi^2 v^2}{l^2}}, \\ k_1' &= -(a+b) - \sqrt{(a-b)^2 - \frac{\pi^2 v^2}{l^2}}. \end{aligned} \quad (17)$$

Hence,

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2} \frac{1}{(p - k_1)(p - k_1')}. \quad (18)$$

By partial fractions equation (18) may be put in another form as follows:

$$\frac{1}{\pi^2 + q^2 l^2} = \frac{v^2}{l^2 (k_1 - k_1')} \left\{ \frac{1}{p - k_1} - \frac{1}{p - k_1'} \right\}. \quad (19)$$

The other terms of equation (12) may be put in a form similar to (19) as follows:

$$\left. \begin{aligned} \frac{1}{(2\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_2 - k_2')} \left\{ \frac{1}{p - k_2} - \frac{1}{p - k_2'} \right\}, \\ \frac{1}{(3\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_3 - k_3')} \left\{ \frac{1}{p - k_3} - \frac{1}{p - k_3'} \right\}, \\ &\dots \dots \dots \\ \frac{1}{(n\pi)^2 + q^2 l^2} &= \frac{v^2}{l^2 (k_n - k_n')} \left\{ \frac{1}{p - k_n} - \frac{1}{p - k_n'} \right\}, \end{aligned} \right\} \quad (20)$$

where

$$\left. \begin{aligned} k_2, k_2' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{2\pi v}{l}\right)^2}, \\ k_3, k_3' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{3\pi v}{l}\right)^2}, \\ &\dots \dots \dots \\ k_n, k_n' &= -(a+b) \pm \sqrt{(a-b)^2 - \left(\frac{n\pi v}{l}\right)^2}. \end{aligned} \right\} \quad (21)$$



Expand each of the terms  $\frac{1}{p-k}$  in a series as follows:

$$\frac{1}{p-k_1} = \frac{1}{p} \left( 1 - \frac{k_1}{p} \right)^{-1} = \frac{1}{p} \left\{ 1 + \frac{k_1}{p} + \frac{k_1^2}{p^2} + \frac{k_1^3}{p^3} + \dots \right\} \quad (22)$$

Operate by this series an  $\epsilon^{j\omega t}$  which is simply successive time integration, the limits of integration being zero and  $t$ . Replace  $j\omega$  by  $\gamma$  for brevity and we get

$$\left. \begin{aligned} \frac{1}{p} \epsilon^{\gamma t} &= \int_0^t \epsilon^{\gamma t} = \frac{1}{\gamma} \epsilon^{\gamma t} - \frac{1}{\gamma} \\ \frac{1}{p^2} \epsilon^{\gamma t} &= \frac{1}{\gamma^2} \epsilon^{\gamma t} - \frac{1}{\gamma^2} - \frac{1}{\gamma} t \\ \frac{1}{p^3} \epsilon^{\gamma t} &= \frac{1}{\gamma^3} \epsilon^{\gamma t} - \frac{1}{\gamma^3} - \frac{1}{\gamma^2} t - \frac{1}{\gamma} \frac{t^2}{2} \\ &\dots\dots\dots \\ \frac{1}{p^n} \epsilon^{\gamma t} &= \frac{1}{\gamma^n} \epsilon^{\gamma t} - \frac{1}{\gamma^n} - \frac{1}{\gamma^{n-1}} t - \frac{1}{\gamma^{n-2}} \frac{t^2}{2} - \dots - \frac{1}{\gamma} \frac{t^{n-1}}{(n-1)} \end{aligned} \right\} \quad (23)$$

Assembling all the terms and arranging them in suitable order, we have

$$\left. \begin{aligned} \frac{1}{p-k_1} \epsilon^{\gamma t} &= \frac{1}{p} \left\{ \epsilon^{\gamma t} \left( 1 + \frac{k_1}{\gamma} + \frac{k_1^2}{\gamma^2} + \frac{k_1^3}{\gamma^3} + \dots \right) \right. \\ &\quad - \frac{k_1}{\gamma} \left( 1 + \frac{k_1}{\gamma} + \frac{k_1^2}{\gamma^2} + \dots \right) \\ &\quad - \frac{k_1}{\gamma} k_1 t \left( 1 + \frac{k_1}{\gamma} + \frac{k_1^2}{\gamma^2} + \dots \right) \\ &\quad \left. - \frac{k_1}{\gamma} \frac{k_1^2 t^2}{2} \left( 1 + \frac{k_1}{\gamma} + \frac{k_1^2}{\gamma^2} + \dots \right) \right. \\ &\quad \left. \dots\dots\dots \right\} \quad (24) \end{aligned} \right\}$$

The above is equivalent to

$$\frac{1}{p-k_1} \epsilon^{\gamma t} = \frac{1}{p} \left\{ \frac{\epsilon^{\gamma t}}{1 - \frac{k_1}{\gamma}} - \frac{k_1}{\gamma} \frac{\epsilon^{k_1 t}}{1 - \frac{k_1}{\gamma}} \right\}. \quad (25)$$

Similarly

$$\frac{1}{p-k_1'} \epsilon^{\gamma t} = \frac{1}{p} \left\{ \frac{\epsilon^{\gamma t}}{1 - \frac{k_1'}{\gamma}} - \frac{k_1'}{\gamma} \frac{\epsilon^{k_1' t}}{1 - \frac{k_1'}{\gamma}} \right\}. \quad (26)$$

Substituting from (25) and (26) into (19) results the relation

$$\frac{1}{\pi^2 + q^2 l^2} \epsilon^{\gamma t} = \frac{v^2}{l^2 (k_1 - k_1')} \frac{1}{p} \left\{ \frac{\gamma \epsilon^{\gamma t}}{\gamma - k_1} - \frac{\gamma \epsilon^{\gamma t}}{\gamma - k_1'} - \frac{k_1 \epsilon^{k_1 t}}{\gamma - k_1} + \frac{k_1' \epsilon^{k_1' t}}{\gamma - k_1'} \right\}. \quad (27)$$

Operating on the bracket term of (27) by  $\frac{1}{p}$ , which is time integration, we get



$$\frac{1}{p} \left\{ \frac{\gamma \epsilon^{\gamma t}}{\gamma - k_1} - \frac{\gamma \epsilon^{\gamma t}}{\gamma - k_1'} - \frac{k_1 \epsilon^{k_1 t}}{\gamma - k_1} + \frac{k_1' \epsilon^{k_1' t}}{\gamma - k_1'} \right\} = \left\{ \frac{\epsilon^{\gamma t}}{\gamma - k_1} - \frac{1}{\gamma - k_1} - \frac{\epsilon^{\gamma t}}{\gamma - k_1'} + \frac{1}{\gamma - k_1'} \right. \\ \left. - \frac{\epsilon^{k_1 t}}{\gamma - k_1} + \frac{1}{\gamma - k_1} + \frac{\epsilon^{k_1' t}}{\gamma - k_1'} - \frac{1}{\gamma - k_1'} \right\} = \epsilon^{\gamma t} \left\{ \frac{1}{\gamma - k_1} - \frac{1}{\gamma - k_1'} \right\} - \frac{\epsilon^{k_1 t}}{\gamma - k_1} + \frac{\epsilon^{k_1' t}}{\gamma - k_1'}. \quad (28)$$

We finally obtain

$$\frac{1}{\pi^2 + q^2 l^2} \epsilon^{\gamma t} = \frac{v^2}{l^2 (k_1 - k_1')} \left\{ \epsilon^{\gamma t} \left( \frac{1}{\gamma - k_1} - \frac{1}{\gamma - k_1'} \right) - \frac{\epsilon^{k_1 t}}{\gamma - k_1} + \frac{\epsilon^{k_1' t}}{\gamma - k_1'} \right\}. \quad (29)$$

It is obvious by inspection that the first part of the bracket term of above equation is exactly of the same form as (19) except that  $p$  is replaced by  $\gamma$ . We may therefore write above equation in the following form:

$$\frac{1}{\pi^2 + q^2 l^2} \epsilon^{\gamma t} = \frac{1}{\pi^2 + s^2 l^2} \epsilon^{\gamma t} + \frac{v^2}{l^2 (k_1 - k_1')} \left\{ \frac{\epsilon^{k_1' t}}{\gamma - k_1'} - \frac{\epsilon^{k_1 t}}{\gamma - k_1} \right\}, \quad (30)$$

where

$$s^2 = \frac{1}{v^2} \left\{ \gamma^2 + 2\gamma(a + b) + 4ab \right\}. \quad (31)$$

Applying the same process to the other terms of equation (12), we shall have:

$$\left. \begin{aligned} \frac{1}{(2\pi)^2 + q^2 l^2} \epsilon^{\gamma t} &= \frac{1}{(2\pi)^2 + s^2 l^2} \epsilon^{\gamma t} + \frac{v^2}{l^2 (k_2 - k_2')} \left\{ \frac{\epsilon^{k_2' t}}{\gamma - k_2'} - \frac{\epsilon^{k_2 t}}{\gamma - k_2} \right\}, \\ \frac{1}{(3\pi)^2 + q^2 l^2} \epsilon^{\gamma t} &= \frac{1}{(3\pi)^2 + s^2 l^2} \epsilon^{\gamma t} + \frac{v^2}{l^2 (k_3 - k_3')} \left\{ \frac{\epsilon^{k_3' t}}{\gamma - k_3'} - \frac{\epsilon^{k_3 t}}{\gamma - k_3} \right\}, \\ &\dots \dots \dots \\ \frac{1}{(n\pi)^2 + q^2 l^2} \epsilon^{\gamma t} &= \frac{1}{(n\pi)^2 + s^2 l^2} \epsilon^{\gamma t} + \frac{v^2}{l^2 (k_n - k_n')} \left\{ \frac{\epsilon^{k_n' t}}{\gamma - k_n'} - \frac{\epsilon^{k_n t}}{\gamma - k_n} \right\}. \end{aligned} \right\} \quad (32)$$

It will be shown presently that the terms in equation (32), which contain the factor  $\epsilon^{\gamma t}$ , are parts of the expression which gives the steady state of the voltage on the line, and the terms containing the factors  $\epsilon^{k_n t}$ ,  $\epsilon^{k_n' t}$  represent the transient part of the voltage. We may consider them separately, designating the part contributing only to the steady state by the subscript  $s$ , and the other part by the subscript  $t$ . Consider first the  $\epsilon^{\gamma t}$  terms, and we have

$$\frac{ql}{\sinh ql} \epsilon^{\gamma t}_{(s)} = \left\{ 1 - 2q^2 l^2 \left( \frac{1}{\pi^2 + s^2 l^2} - \frac{1}{(2\pi)^2 + s^2 l^2} + \dots \right) \right\} \epsilon^{\gamma t} \quad (33)$$

Operating by  $q^2 l^2$  on  $\epsilon^{\gamma t}$  involves complete differentiation which in this case would only change the  $p$ 's to  $\gamma$ 's in the  $q$  expression and consequently change  $q^2 l^2$  to  $s^2 l^2$ , hence



$$\frac{ql}{\text{Sinh } ql} \epsilon^{\gamma t} = \left\{ 1 - 2s^2 l^2 \left( \frac{1}{\pi^2 + s^2 l^2} - \frac{1}{(2\pi)^2 + s^2 l^2} + \frac{1}{(3\pi)^2 + s^2 l^2} - \dots \right) \right\} \epsilon^{\gamma t} \\ = \frac{sl}{\text{Sinh } sl} \epsilon^{\gamma t}. \quad (34)$$

To get the complete solution for the steady voltage, we must now operate on (34) by the factor  $\frac{\text{Sinh } q(l-x)}{ql}$ , see equation (11).

Now

$$\frac{\text{Sinh } q(l-x)}{ql} = q(l-x) + \frac{q^3(l-x)^3}{\underline{3}} + \frac{q^5(l-x)^5}{\underline{5}} + \dots \\ = \left( 1 - \frac{x}{l} \right) + \frac{q^2 \left( 1 - \frac{x}{l} \right)^3}{\underline{3}} + \frac{q^4 \left( 1 - \frac{x}{l} \right)^5}{\underline{5}} + \dots \quad (35)$$

Again the  $q$  terms in this case involve only complete differentiation, which in operating on  $\epsilon^{\gamma t}$  changes the  $p$  to  $\gamma$  and therefore the  $q$  to  $s$  in equation (35) which gives

$$\frac{\text{Sinh } q(l-x)}{ql} \epsilon^{\gamma t} = \frac{\text{Sinh } s(l-x)}{sl} \epsilon^{\gamma t}. \quad (36)$$

Combining (34) and (36) we get for the following expression for the steady voltage on the line:

$$V_s = \frac{E \text{Sinh } s(l-x)}{\text{Sinh } sl} \epsilon^{\gamma t}. \quad (37)$$

Replacing  $\gamma$  by  $j\omega$ , we have

$$V_s = \frac{E \text{Sinh } s(l-x)}{\text{Sinh } sl} \epsilon^{j\omega t}, \\ s^2 = (Lj\omega + R)(Cj\omega + g). \quad (38)$$

The above is the well-known solution for the steady state and is obvious from (10). The derivation of (38) is incidental, the main purpose of this paper being the study of the transient effects which occur during the establishment of the steady state. Referring to equations (12), (30) and (32), we find that remaining terms of the expansion  $\frac{ql}{\text{Sinh } ql}$  operated on  $\epsilon^{\gamma t}$  are as follows:

$$\frac{ql}{\text{Sinh } ql} \epsilon^{\gamma t} = -2q^2 l^2 \left\{ \frac{\tau^2}{l^2(k_1 - k_1')} \left( \frac{\epsilon^{k_1' t}}{\gamma - k_1'} - \frac{\epsilon^{k_1 t}}{\gamma - k_1} \right) \right. \\ - \frac{\tau^2}{l^2(k_2 - k_2')} \left( \frac{\epsilon^{k_2' t}}{\gamma - k_2'} - \frac{\epsilon^{k_2 t}}{\gamma - k_2} \right) \\ + \frac{\tau^2}{l^2(k_3 - k_3')} \left( \frac{\epsilon^{k_3' t}}{\gamma - k_3'} - \frac{\epsilon^{k_3 t}}{\gamma - k_3} \right) \\ \left. - \dots \dots \dots \right\}, \quad (39)$$



and the above expression is again to be operated on by  $E \frac{\text{Sinh } q(l-x)}{ql}$  to get the expression for  $V_t$  the transient voltage on the line. The term  $\frac{\text{Sinh } q(l-x)}{ql}$  multiplied by  $q^2 l^2$ , the factor in the right-hand side of equation (39), may be expressed in a series as follows:

$$\frac{q^2 l^2 \text{Sinh } q(l-x)}{ql} = q^2 l^2 \left(1 - \frac{x}{l}\right) + \frac{q^4 l^4}{13} \left(1 - \frac{x}{l}\right)^3 + \frac{q^6 l^6}{15} \left(1 - \frac{x}{l}\right)^5 + \dots \quad (40)$$

Operating by (40) on each one of the terms of (39) involves complete differentiation and will only change the  $p$ 's in the  $q$  expression to  $k_1, k'_1, k_2, k'_2, k_3, k'_3$ , etc.

That is, operating by  $ql \text{Sinh } q(l-x)$  on  $\epsilon^{k_1 t}$  gives

$$ql \text{Sinh } q(l-x) \epsilon^{k_1 t} = m_1 l \text{Sinh } m_1(l-x) \epsilon^{k_1 t}, \quad (41)$$

where

$$m_1^2 = \frac{1}{v^2} \left\{ k_1^2 + 2k_1(a+b) + 4ab \right\}. \quad (42)$$

Operating in the same way on all the other terms of equation (39), we get

$$\begin{aligned} V_t = & -2E \frac{v^2}{l^2} \left\{ \frac{1}{k_1 - k'_1} \left[ \frac{m'_1 l \text{Sinh } m'_1(l-x)}{\gamma - k'_1} \epsilon^{k'_1 t} - \frac{m_1 l \text{Sinh } m_1(l-x)}{\gamma - k_1} \epsilon^{k_1 t} \right] \right. \\ & - \frac{1}{k_2 - k'_2} \left[ \frac{m'_2 l \text{Sinh } m'_2(l-x)}{\gamma - k'_2} \epsilon^{k'_2 t} - \frac{m_2 l \text{Sinh } m_2(l-x)}{\gamma - k_2} \epsilon^{k_2 t} \right] \\ & + \frac{1}{k_3 - k'_3} \left[ \frac{m'_3 l \text{Sinh } m'_3(l-x)}{\gamma - k'_3} \epsilon^{k'_3 t} - \frac{m_3 l \text{Sinh } m_3(l-x)}{\gamma - k_3} \epsilon^{k_3 t} \right] \\ & \left. - \dots \dots \dots \right\} \quad (43) \end{aligned}$$

The values of  $k_1, k'_1, k_2, k'_2, k_3, k'_3$ , etc., are given by equations (17) and (21) and may be put in the following form:

$$\left. \begin{aligned} k_1 &= -\alpha + j\beta_1, \\ k'_1 &= -\alpha - j\beta_1, \\ k_2 &= -\alpha + j\beta_2, \\ k'_2 &= -\alpha - j\beta_2, \\ &\dots \dots \dots \\ k_n &= -\alpha + j\beta_n, \\ k'_n &= -\alpha - j\beta_n, \end{aligned} \right\} \quad (44)$$

where

$$\alpha = a + b$$

$$\beta_n = \sqrt{\left(\frac{n\pi v}{l}\right)^2 - (a-b)^2} \quad (45)$$

Substituting for the value of  $k$  from (44) into (42), we get



$$m_1^2 = \frac{1}{v^2} \left\{ \alpha^2 - \beta_1^2 - 2\alpha j\beta_1 - 2\alpha^2 + 2\alpha j\beta_1 + 4ab \right\} \\ = \frac{1}{v^2} \left\{ -\alpha^2 - \beta_1^2 + 4ab \right\}$$

Substituting the values of  $\alpha$  and  $\beta$  from (45), we get

$$m_1^2 = -\frac{\pi^2}{l^2}. \quad (46)$$

Similarly we find

$$\left. \begin{aligned} m_1'^2 &= -\frac{\pi^2}{l^2}, \\ m_2^2 = m_2'^2 &= -\left(\frac{2\pi}{l}\right)^2, \\ m_3^2 = m_3'^2 &= -\left(\frac{3\pi}{l}\right)^2, \\ &\dots \dots \dots \end{aligned} \right\} \quad (47)$$

We also have

$$\left. \begin{aligned} k_1 - k_1' &= 2j\beta_1, \\ k_2 - k_2' &= 2j\beta_2, \\ &\dots \dots \dots \\ k_n - k_n' &= 2j\beta_n. \end{aligned} \right\} \quad (48)$$

Substituting the values from (47) and (48) in (43) and using the relation

$$\text{Sinh } jx = j \text{ Sin } x,$$

equation (43) reduces to the following:

$$V_t = -E \frac{v^2}{l^2} e^{-\alpha t} \left\{ \frac{\pi}{\beta_1} j \text{ Sin } \pi \left(1 - \frac{x}{l}\right) \left[ \frac{e^{-j\beta_1 t}}{\gamma + \alpha + j\beta_1} - \frac{e^{j\beta_1 t}}{\gamma + \alpha - j\beta_1} \right] \right. \\ - \frac{2\pi}{\beta_2} j \text{ Sin } 2\pi \left(1 - \frac{x}{l}\right) \left[ \frac{e^{-j\beta_2 t}}{\gamma + \alpha + j\beta_2} - \frac{e^{j\beta_2 t}}{\gamma + \alpha - j\beta_2} \right] \\ \dots \dots \dots \\ \left. \pm \frac{n\pi}{\beta_n} j \text{ Sin } n\pi \left(1 - \frac{x}{l}\right) \left[ \frac{e^{-j\beta_n t}}{\gamma + \alpha + j\beta_n} - \frac{e^{j\beta_n t}}{\gamma + \alpha - j\beta_n} \right] \right\}. \quad (49)$$

The above may be further simplified. Replacing  $\gamma$  by  $j\omega$ , we have

$$\frac{e^{-j\beta_1 t}}{\alpha + j(\omega + \beta_1)} - \frac{e^{j\beta_1 t}}{\alpha + j(\omega - \beta_1)} \\ = \frac{(\alpha + j\omega - j\beta_1)(\text{Cos } \beta_1 t - j \text{ Sin } \beta_1 t) - (\alpha + j\omega + j\beta_1)(\text{Cos } \beta_1 t + j \text{ Sin } \beta_1 t)}{(\alpha^2 + \beta_1^2 - \omega^2) + 2j\omega\alpha} \\ = \frac{2 \left\{ (\omega - \alpha j) \text{ Sin } \beta_1 t - j\beta_1 \text{ Cos } \beta_1 t \right\}}{\alpha^2 - \beta_1^2 - \omega^2 + 2j\omega\alpha}$$



Using only the imaginary part, so that when multiplied by the imaginary factor  $j$  in equation (49) will give the real part of (49), we get

$$\frac{\varepsilon^{-j\beta_1 t}}{\alpha + j\omega + j\beta_1} - \frac{\varepsilon^{j\beta_1 t}}{\alpha + j\omega - j\beta_1} \left( \begin{array}{c} \text{imaginary} \\ \text{part} \end{array} \right) = \frac{j \sin(\beta_1 t + \varphi_1)}{K_1}, \quad (50)$$

where

$$K_1 = \sqrt{\frac{(\alpha^2 + \beta_1^2 - \omega^2)^2 + 4\alpha^2\omega^2}{\alpha^2 + \beta_1^2}}, \quad (51)$$

$$\tan \varphi_1 = \frac{\beta_1(\alpha^2 + \beta_1^2 - \omega^2)}{\alpha(\alpha^2 + \beta_1^2 + \omega^2)},$$

and similar transformations for all the other terms in (49), using different  $\beta$ 's;  $\beta_2, \beta_3, \beta_4$ , etc., for the other terms.

Substituting from (51) in (49), we finally get for  $V_t$  the transient voltage on the line

$$\begin{aligned} V_t = -E \frac{v^2}{l^2} \varepsilon^{-\alpha t} & \left\{ \frac{\pi}{\beta_1 K_1} \sin \pi \left( 1 - \frac{x}{l} \right) \sin(\beta_1 t + \varphi_1) \right. \\ & - \frac{2\pi}{\beta_2 K_2} \sin 2\pi \left( 1 - \frac{x}{l} \right) \sin(\beta_2 t + \varphi_2) \\ & + \frac{3\pi}{\beta_3 K_3} \sin 3\pi \left( 1 - \frac{x}{l} \right) \sin(\beta_3 t + \varphi_3) \\ & \left. - \dots \dots \dots \right\} \end{aligned} \quad (52)$$

or

$$V_t = E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{\beta_n K_n} \sin n\pi \left( 1 - \frac{x}{l} \right) \sin(\beta_n t + \varphi_n). \quad (53)$$

Combining the above with equation (38) we get the complete expression for the voltage at any point on the line and at any time ( $t$ ) after the application of the e.m.f. The component given by (38) represents the steady state, and the component given by (53) represents the transient state. The complete expression is

$$\begin{aligned} V = V_s + V_t = \frac{E \sinh s(l-x)}{\sinh sl} \varepsilon^{j\omega t} + E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{\beta_n K_n} \\ \sin n\pi \left( 1 - \frac{x}{l} \right) \sin(\beta_n t + \varphi_n). \end{aligned} \quad (54)$$

Only the real part of the first term of the right-hand member of above equation to be used.

The expression for the current distribution on the line is easily derived from (54) by the aid of either of equations (1). Use the second equation:

$$-\frac{dI}{dx} = C \frac{dV}{dt} + gV.$$



Using the expression for  $V$  given by (54), we have

$$\begin{aligned}
 -\frac{dI}{dx} &= (Cj\omega + g) E \frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} \\
 &+ CE \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{K_n} \text{Sin } n\pi \left(1 - \frac{x}{l}\right) \text{Sin } (\beta_n t + \varphi_n) \\
 &- CE\alpha \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{\beta_n K_n} \text{Sin } n\pi \left(1 - \frac{x}{l}\right) \text{Sin } (\beta_n t + \varphi_n) \\
 &+ gE \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{\beta_n K_n} \text{Sin } n\pi \left(1 - \frac{x}{l}\right) \text{Sin } (\beta_n t + \varphi_n).
 \end{aligned} \quad (55)$$

Combining the summation terms, we get

$$\begin{aligned}
 -\frac{dI}{dx} &= (Cj\omega + g) E \frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} + E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{K_n} \text{Sin } n\pi \left(1 - \frac{x}{l}\right) \\
 &\quad \left\{ C \cos (\beta_n t + \varphi_n) + \frac{(g-\alpha)}{\beta_n} \text{Sin } (\beta_n t + \varphi_n) \right\} \\
 &= (Cj\omega + g) E \frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} + E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{n\pi}{K_n} \sqrt{C^2 + \frac{(g-\alpha)^2}{\beta^2}} \\
 &\quad \text{Sin } n\pi \left(1 - \frac{x}{l}\right) \text{Cos } (\beta_n t + \varphi_n - \psi_n). \\
 &\quad \tan \psi_n = \frac{g-\alpha C}{\beta_n}.
 \end{aligned} \quad (56)$$

Integrating the above with respect to  $x$ , we get the expression for the current on the line as follows:

$$\begin{aligned}
 I &= \frac{Cj\omega + g}{s} E \frac{\text{Cosh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} - E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{\infty} (-1)^n \frac{l}{K_n} \sqrt{C^2 + \frac{(g-\alpha)^2}{\beta_n^2}} \\
 &\quad \text{Cos } n\pi \left(1 - \frac{x}{l}\right) \text{Cos } (\beta_n t + \varphi_n - \psi_n).
 \end{aligned} \quad (57)$$

The above equations (54) and (57) are the general expressions for the voltage and current distribution on the line for an impressed electromotive force of any frequency, one component in the expressions giving the steady state voltage and current on the line, and the other the transient voltage and current, the latter subsiding exponentially. Consider now special cases.

#### CONSTANT E.M.F.

For a constant e.m.f. zero frequency, we have  $s^2 = Rg$ , which is an extremely small quantity, and we may therefore write:

$$\frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} = \frac{s(l-x)}{sl} = 1 - \frac{x}{l}. \quad (58)$$



Also by (51) putting  $\omega = 0$ , we have

$$\left. \begin{aligned} K_1 = K_2 = K_3 = \dots K_n = \sqrt{\alpha^2 + \beta^2} \\ \tan \varphi_n = \frac{\beta_n}{\alpha} \end{aligned} \right\} \quad (59)$$

Substituting in (54) and (57), we get

$$\begin{aligned} V = V_s + V_t = E \left( 1 - \frac{x}{l} \right) + \\ E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{n=\infty} (-1)^n \frac{n\pi}{\beta_n} \sin n\pi \left( 1 - \frac{x}{l} \right) \sin (\beta_n t + \varphi_n). \quad (60) \\ I = E \sqrt{\frac{g}{R}} \frac{\cosh s(l-x)}{\sinh s l} - E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \\ \sum_{n=1}^{n=\infty} (-1)^n l \sqrt{\frac{C^2 + \frac{(g-\alpha C)^2}{\beta_n^2}}{K_n}} \cos n\pi \left( 1 - \frac{x}{l} \right) \cos (\beta_n t + \varphi_n - \psi_n). \quad (61) \end{aligned}$$

when  $g$  is very small

$$\frac{\cosh s(l-x)}{\sinh s l} = \frac{1}{s l} = \frac{1}{\sqrt{R g l}}$$

and the above reduces to

$$I = \frac{E}{R l} - E \frac{v^2}{l^2} \varepsilon^{-\alpha t} \sum_{n=1}^{n=\infty} (-1)^n l \sqrt{\frac{C^2 + \frac{(g-\alpha C)^2}{\beta_n^2}}{K_n}} \cos n\pi \left( 1 - \frac{x}{l} \right) \cos (\beta_n t + \varphi_n - \psi_n). \quad (62)$$

In equations (54), (57), (60) and (61) the factor

$$\varepsilon^{-\alpha t} = \varepsilon^{-\frac{1}{2} \left( \frac{R}{L} + \frac{g}{C} \right) t}$$

determines the time rate at which the transient components of the voltage and current die out.

#### OCEAN CABLE.

From equations (54) and (57) the expressions for the voltage and current distribution on an ocean telegraph cable may be readily derived. In an ocean cable the inductance and leakage are negligible, it is assumed that  $L = 0$  and  $g = 0$ . In this case we have by (21),



$$\begin{aligned}
 k_n &= -a + \sqrt{a^2 - \frac{n^2 \pi^2 v^2}{l^2}}, \\
 k'_n &= -a - \sqrt{a^2 - \frac{n^2 \pi^2 v^2}{l^2}}, \\
 a^2 &= \frac{R^2}{4L^2}, v^2 = \frac{1}{LC}.
 \end{aligned} \tag{63}$$

For negligible inductance  $a^2$  is very large in comparison with  $\frac{\pi^2 v^2}{l^2}$ , and we may therefore put

$$\begin{aligned}
 k_n &= -a + a \left(1 - \frac{n^2 \pi^2 v^2}{l^2}\right)^{1/2} = -a + a \left(1 - \frac{1}{2} \frac{n^2 \pi^2 v^2}{a^2 l^2}\right) \\
 &= -\frac{1}{2} \frac{n^2 \pi^2 v^2}{a l^2} = -\frac{n^2 \pi^2}{R C l^2}.
 \end{aligned} \tag{64}$$

Similarly

$$k'_n = -a - a \left(1 - \frac{1}{2} \frac{n^2 \pi^2 v^2}{a^2 l^2}\right)^{1/2} = 2a = -\infty \text{ for } L = 0 \tag{65}$$

and

$$\epsilon^{k'_n t} = 0$$

Also  $k_1, k_2, \dots, k_n$ , etc., are negligible in comparison with  $k'_1, k'_2, \dots, k'_n$ , etc., respectively.

Substituting the values from above equations in (43), we have

$$\begin{aligned}
 V_t = -\frac{2E}{2a} \frac{v^2}{l^2} \left\{ \frac{-m_1 l \sinh m_1 (l-x)}{\gamma - k_1} \epsilon^{-\frac{\pi^2}{R C l^2} t} + \frac{m_2 l \sinh m_2 (l-x)}{\gamma - k_2} \epsilon^{-\frac{(2\pi)^2}{R C l^2} t} \right. \\
 \left. - \frac{m_3 l \sinh m_3 (l-x)}{\gamma - k_3} \epsilon^{-\frac{(3\pi)^2}{R C l^2} t} + \dots \right\} \tag{66}
 \end{aligned}$$

Replacing  $m_1, m_2, m_3$ , etc., by the corresponding values  $j\frac{\pi}{l}, j\frac{2\pi}{l}, j\frac{3\pi}{l}$ , etc., and  $\gamma$  by  $j\omega$ , the above becomes

$$\begin{aligned}
 V_t &= -\frac{2E}{R C l^2} \left\{ \frac{\pi \sin \pi \left(1 - \frac{x}{l}\right)}{j\omega + \frac{\pi^2}{R C l^2}} \epsilon^{-\frac{\pi^2}{R C l^2} t} - \frac{2\pi \sin 2\pi \left(1 - \frac{x}{l}\right)}{j\omega + \frac{(2\pi)^2}{R C l^2}} \epsilon^{-\frac{(2\pi)^2}{R C l^2} t} + \dots \right\} \\
 &= \frac{2E\pi}{R C l^2} \sum_{n=1}^{\infty} (-1)^n \frac{n \sin n\pi \left(1 - \frac{x}{l}\right)}{j\omega + \frac{(n\pi)^2}{R C l^2}} \epsilon^{-\frac{(n\pi)^2}{R C l^2} t} \tag{67}
 \end{aligned}$$

For the steady state we have by (38)

$$V_s = \frac{E \sinh s(l-x)}{\sinh sl} \epsilon^{j\omega t},$$



but in this case

$$s^2 = RCj\omega.$$

The complete expression for the voltage on the cable for a sinusoidal e.m.f. of frequency  $\frac{\omega}{2\pi}$  impressed on the cable is

$$V = V_s + V_t = E \frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} + \frac{2E\pi}{RCl^2} \sum_{n=1}^{\infty} (-1)^n \frac{n \sin n\pi \left(1 - \frac{x}{l}\right)}{j\omega + \frac{(n\pi)^2}{RCl^2}} \varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}}. \quad (68)$$

The expression for the current on the cable may be derived in similar manner from equation (57), but can be more directly obtained from (68). For  $L = 0$ , we have the relation

$$RI = -\frac{dV}{dx},$$

and

$$I = \frac{Es}{R} \frac{\text{Cosh } s(l-x)}{\text{Sinh } sl} \varepsilon^{j\omega t} - \frac{2E\pi^2}{RCl^2} \sum_{n=1}^{\infty} (-1)^n \frac{n^2 \cos n\pi \left(1 - \frac{x}{l}\right)}{Rl \left(j\omega + \frac{(n\pi)^2}{RCl^2}\right)} \varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}} \quad (69)$$

For a constant e.m.f.,  $\omega = 0$

$$\frac{\text{Sinh } s(l-x)}{\text{Sinh } sl} = 1 - \frac{x}{l}, \quad \frac{\text{Cosh } s(l-x)}{\text{Sinh } sl} = \frac{1}{sl}$$

and equations (68) and (69) reduce to

$$V = E \left(1 - \frac{x}{l}\right) + 2E \sum_{n=1}^{\infty} (-1)^n \frac{\sin n\pi \left(1 - \frac{x}{l}\right)}{n\pi} \varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}} \quad (70)$$

$$I = \frac{E}{Rl} - \frac{2E}{Rl} \sum_{n=1}^{\infty} (-1)^n \cos n\pi \left(1 - \frac{x}{l}\right) \varepsilon^{-\frac{(n\pi)^2 t}{RCl^2}}. \quad (71)$$

Equations (70) and (71) are the well-known solutions of the telegraphic equation which was first given by Lord Kelvin in 1855 and has since been studied by other investigators. It is seen that by the use of the method developed in this paper, the solution of the telegraphic equation is but a special case of the general solution given by equations (54) and (57). Even for the cable telegraph problem we have by this method arrived at a more comprehensive solution, equations (68) and (69), which are applicable for alternating and direct voltages, reducing to (70) and (71) when the frequency is zero.



# THE CRYSTAL STRUCTURE OF BISMUTH.\*

BY

L. W. McKEEHAN, Ph.D.

Research Laboratories of the American Telephone and Telegraph Company, and the Western Electric Company, Incorporated.

THE electrical and magnetic properties of metallic bismuth are in many respects so peculiar that an exact knowledge of its crystal structure seems important in any attempt to correlate these properties for metals in general. The work of previous investigators of the structure has accordingly been reviewed, and some additional data obtained as opportunity offered.

The spectrometric method was used by Ogg,<sup>1</sup> who obtained reflections of palladium X-rays from the (111) and (200) planes, and by James,<sup>2</sup> who obtained reflections of rhodium X-rays from the same planes and from the (11 $\bar{1}$ ) planes in addition. The nomenclature of planes depends upon the choice of crystallographic axes, and both of the investigators referred to employed rhombohedral axes mutually inclined at  $87^{\circ}-34'$ , as given by the standard handbooks of crystallography. With this choice of axes the units of structure are face-centred rhombohedra which differ but little from cubes. Two such lattices must be present, and are so situated with respect to each other that the whole array of points is not much different from a simple cubic lattice.

The face-centred rhombohedral space-lattice is not, however, recognized as a fundamental type. Simplicity in nomenclature is attained by using instead of the above-described axes a set of rhombohedral axes which are halves of the face-diagonals of the rhombohedron first chosen, and which are therefore mutually inclined at  $57^{\circ}-16'$ . The corresponding space-lattice is simple rhombohedral, a fundamental type ( $\Gamma_{rh}$ ). It will be noticed that the longest body diagonal of a cell of either of these space-lattices has the same length. Quantities and symbols referred to the simpler axes will be indicated in what follows by the use of primes. Formulæ for transforming the indices of planes have been given

---

\* Communicated by Gen. John J. Carty, E.D., Associate Editor of this JOURNAL.

<sup>1</sup> A. Ogg, *Phil. Mag.*, (6), 42, 163-166, July, 1921.

<sup>2</sup> R. W. James, *Phil. Mag.*, (6), 42, 193-196, July, 1921.



by Wyckoff <sup>3</sup> who was forced to use a similar artifice in analyzing the structure of calcite.

Table I summarizes the data referred to above, and the results computed from currently accepted X-ray wave-lengths.<sup>4</sup> The results are seen to be in as good agreement as the indicated accuracy in angular measurements would lead one to expect. The mean value

$a = 6.546 \times 10^{-8}$  cm. ( $a' = 4.726 \times 10^{-8}$  cm.)

corresponds to a density of 9.863 gm./cm.<sup>3</sup> which is not unreason-

TABLE I.

Observer X-rays of Effective Wave-length <sup>4</sup>		Ogg <sup>1</sup> Palladium $0.588 \times 10^{-8}$ cm. $10^8 \times$			James <sup>2</sup> Rhodium $0.614 \times 10^{-8}$ cm. $10^8 \times$		
Planes		$\theta$	$a$	$a'$	$\theta$	$a$	$a'$
(111)	(111)'	4°-18'	6.520	4.708	4°-29'	6.531	4.715
(11 $\bar{1}$ )	(100)'				4°-45'	6.519	4.707
(200)	(110)'	5°-08'	6.583	4.753	5°-25'	6.516	4.704
(222)	(222)'				8°-54'	6.600	4.765
(22 $\bar{2}$ )	(200)'				9°-27'	6.576	4.748
(400)	(220)'				10°-52'	6.525	4.711
(333)	(333)'				13°-26'	6.592	4.759
(600)	(330)'				16°-20'	6.497	4.690
Mean values			6.55	4.73		6.544	4.725

<sup>1</sup> A. Ogg, *Phil. Mag.*, (6), 42, 163-166, July, 1921.  
<sup>2</sup> R. W. James, *Phil. Mag.*, (6), 42, 193-196, July, 1921.  
<sup>4</sup> W. Duane, *Nat. Res. Counc. Bull.*, 1, 383-408, Nov., 1920.

ably high, considering the improbability of perfect fit between the individual crystallites in massive samples.<sup>5</sup>

James found that the points of one lattice lie on the trigonal axes through the points of the other, not quite at the centres of the rhombohedra. Recalculating from his data his result is confirmed, the ratio of intensities for the first three orders of reflection from the (111) planes agreeing with a displacement of either lattice from the body-centred position in the other by  $(0.306 \pm 0.033) \times 10^{-8}$  cm. In terms of the two sets of axes

<sup>3</sup> R. W. G. Wyckoff, *Amer. Jour. Sci.*, (4), 50, 317-360, Nov., 1920.  
<sup>4</sup> W. Duane, *Nat. Res. Counc. Bull.*, 1, 383-408, Nov., 1920.  
<sup>5</sup> The density is calculated from  $a' = 4.726 \times 10^{-8}$  cm.,  $a' = 57^\circ - 16'$ , using the following constants: atomic weight of bismuth, 209.0; number of molecules per gram molecule,  $6.0594 \times 10^{23}$ , the latter being taken from Birge, *Phys. Rev.*, (2), 14, 365, (1919).



TABLE II.

Film No. s =	90	96	102	105	130	147	152	159	225	407
	3.60							3.62		
	4.14									
	4.24									
	4.34									
		4.35								
		4.36								
						4.42	4.39	4.39		4.39
		4.44	4.44	4.44						
					4.45					
	6.00	5.90								
										6.02
			6.12				6.11	6.06	6.11	
						6.14				
				6.36				6.32		
			6.38							6.37
								6.39		
	7.10				6.45					
							7.13			
							7.34	7.30		
		7.38								
									7.39	
	7.51					7.40				
		7.57								
								7.71		7.76
				7.80				8.83		8.85
							8.86			
			8.88							
				8.91		8.89				
	9.25									
								9.30		
	9.38					9.31				
		9.40								
	9.55									
								9.72		
							9.75			9.74
	9.84									
										10.07
		10.14		10.14			10.10			
					10.20					



TABLE II (*Continued*).

Film No.	90	96	102	105	130	147	152	159	225	407
$s =$		10.50						10.50		
		10.58					10.52			
								10.95		10.93
							10.97			
	11.10									
		11.12								
		11.52		11.19						
		12.80								
		12.88					12.86	12.86		
				12.91						
	13.12									
	14.00									
				14.08						
	14.20									
		15.14		15.14						
		15.34								
	15.69									
	17.03									
	18.31									
	20.10									
	20.77									
	21.90									
	24.29									

the representative points, those absorbed by a single rhombohedron, are accordingly:

$$(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2}), \text{ and } (u, u, u), (u + \frac{1}{2}, u + \frac{1}{2}, u), (u + \frac{1}{2}, u, u + \frac{1}{2}), (u, u + \frac{1}{2}, u + \frac{1}{2});$$

or

$$(0, 0, 0)', \text{ and } (u, u, u)'. \text{ In either case } u = 0.474 \pm 0.003.$$

New data were taken by the powder method, using X-rays of molybdenum, and only the larger crystals of the ground samples seemed to be sufficiently perfect to give good reflections, so that the photographs obtained consisted of widely separated spots, many possible reflections not being observed at all. The data are summarized in Table II. Under these conditions the most direct way of comparing the new data with the old was to calculate the position,  $s$ , and intensity,  $i$ , of the reflections to be expected from a random distribution of crystals having the previously determined structure, and to compare the position and frequency of occurrence of spots on the new photographs with this expected



TABLE III.

(hkl)	(hkl)'	log (d $\times 10^3$ )	s	i
111	111	0.59518	3.69	88
11 $\bar{1}$	100	0.57085	3.90	9
200	110	0.51421	4.44	1000
220	211	0.37275	6.17	480
20 $\bar{2}$	10 $\bar{1}$	0.35501	6.43	493
311	221	0.30613	7.20	62
22 $\bar{2}$	222	0.29415	7.40	290
31 $\bar{1}$	210	0.29294	7.43	22
31 $\bar{1}$	11 $\bar{1}$	0.28663	7.54	2
22 $\bar{2}$	200	0.26982	7.84	324
200	220	0.21319	8.94	230
331	322	0.19033	9.44	68
33 $\bar{1}$	311	0.17869	9.70	35
420	321	0.17194	9.85	165
31 $\bar{3}$	20 $\bar{1}$	0.16763	9.95	1
40 $\bar{2}$	21 $\bar{1}$	0.15775	10.19	194
42 $\bar{2}$	332	0.14044	10.61	116
42 $\bar{2}$	310	0.12220	11.08	151
333	333	0.11806	11.19	75
42 $\bar{2}$	21 $\bar{1}$	0.11645	11.23	164
511	331	0.10691	11.49	46
51 $\bar{1}$	320	0.09891	11.70	24
{51 $\bar{1}$ }	{22 $\bar{1}$ }	{0.09373}	{11.85}	{9}
{333}	{300}	{0.09375}	{11.85}	{9}
440	422	0.07172	12.49	84
531	432	0.05519	12.99	56
404	20 $\bar{2}$	0.05397	13.02	123
442	433	0.05345	13.04	58
53 $\bar{1}$	421	0.04679	13.25	35
{600}	{330}	{0.03709}	{13.56}	{89}
{442}	{411}	{0.03709}	{13.56}	{89}
51 $\bar{3}$	31 $\bar{1}$	0.03672	13.57	7
51 $\bar{3}$	21 $\bar{2}$	0.03476	13.63	1
424	30 $\bar{1}$	0.02935	13.81	107
620	431	0.01960	14.14	66
533	443	0.01522	14.29	63
602	32 $\bar{1}$	0.00896	14.50	90
622	442	0.00511	14.64	46
533	410	9.99483	15.01	15
444	444	9.99312	15.07	29
622	420	9.99191	15.11	72
533	31 $\bar{1}$	9.99001	15.18	1
622	22 $\bar{2}$	9.98560	15.34	88
551	533	9.97398	15.78	52
444	400	9.96879	15.98	75
{711}	{441}	{9.96674}	{16.06}	{37}
{551}	{522}	{9.96674}	{16.06}	{37}
640	532	9.96558	16.11	38
71 $\bar{1}$	430	9.96111	16.28	24
71 $\bar{1}$	33 $\bar{1}$	9.95699	16.45	12
642	543	9.95555	16.50	24
515	30 $\bar{2}$	9.95293	16.61	1
604	31 $\bar{2}$	9.94921	16.76	74
553	544	9.94701	16.85	57
642	521	9.94242	17.04	47



TABLE III (*Continued*).

( <i>hkl</i> )	( <i>hkl</i> )'	$\log(dx10^8)$	<i>s</i>	<i>i</i>
73 $\bar{1}$	542	9.93934	17.17	45
624	41 $\bar{1}$	9.93491	17.36	64
73 $\bar{1}$	53 $\bar{1}$	9.93315	17.44	32
624	312	9.93246	17.46	70
553	51 $\bar{1}$	9.92832	17.65	20
713	42 $\bar{1}$	9.92477	17.80	11
{713	{322	{9.92243	{17.90	{4
{535	{401	{9.92243	{17.90	{4
644	554	9.91635	18.17	11
733	553	9.91614	18.18	50
800	440	9.91215	18.36	40
820	541	9.90320	18.77	29
733	520	9.89983	18.93	18
555	555	9.89621	19.10	53
{882	{552	{9.89563	{19.13	{18
{660	{633	{9.89563	{19.13	{18
{802	{451	{9.89485	{19.17	{46
{644	{510	{9.89485	{19.17	{46
733	322	9.89365	19.23	0
644	41 $\bar{1}$	9.89080	19.36	57
662	644	9.88931	19.43	10
751	643	9.88912	19.44	44
822	530	9.88559	19.62	36
751	632	9.88322	19.73	34
822	332	9.87979	19.90	50
606	303	9.87789	20.00	55
662	622	9.87765	20.01	26
555	500	9.87188	20.30	8

distribution of reflections. Table III contains the results of such calculations for the particular apparatus employed, the reduction from the logarithm of the parameter of a set of planes to the length in centimetres of the arc of deviation involving the wavelength of the X-rays,  $0.712 \times 10^{-8}$  cm. (palladium  $K\alpha_1$ ) and the radius of the film-holder, 20.36 cm. The calculations are carried out for all plane-spacings and orders of reflection which could give reflected spots within about twenty centimetres of the undeflected spot.<sup>6</sup>

The results contained in Tables II and III are better exhibited for comparison in Fig. 1, where the abscissa is the arc length, *s*, in centimetres. Vertical lines of a length proportional to the intensities given in Table III are drawn at the appropriate values of *s*, and the locations of spots listed in Table II are indicated by dots, those on any horizontal line belonging to a single photograph.

<sup>6</sup> The intensity is proportional to  $\cos^2 \pi u (h + k + l)'$ . Cf. R. W. G. Wyckoff, *loc. cit.*<sup>3</sup>



The complexity of the expected pattern makes an interpretation of the observed discrepancies somewhat difficult. It can be stated, however, that the structure of a single lattice is checked better

FIG. 1.

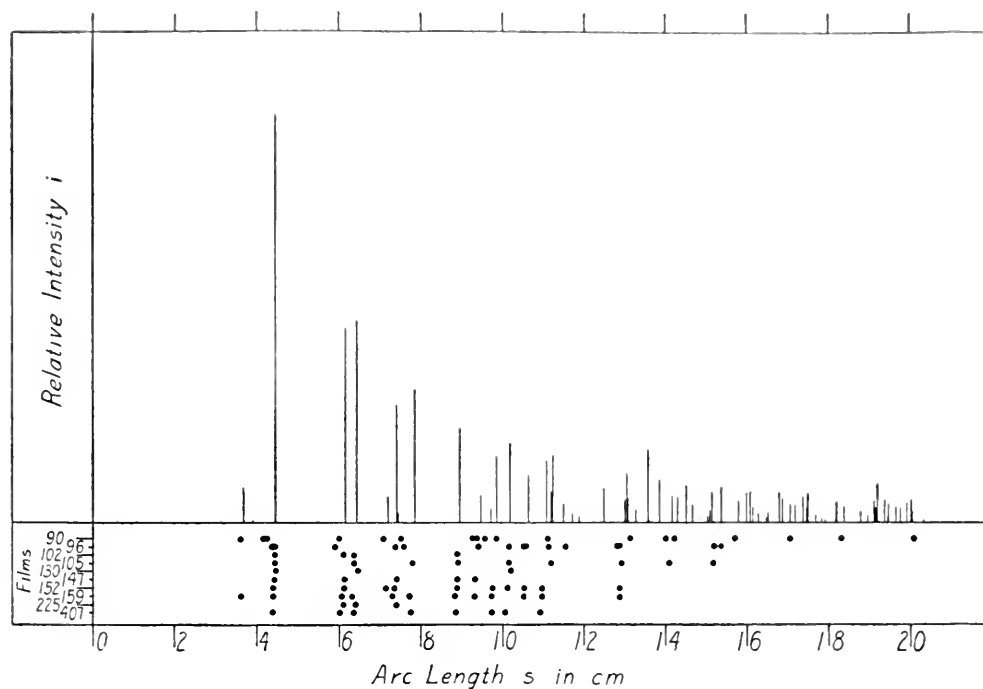
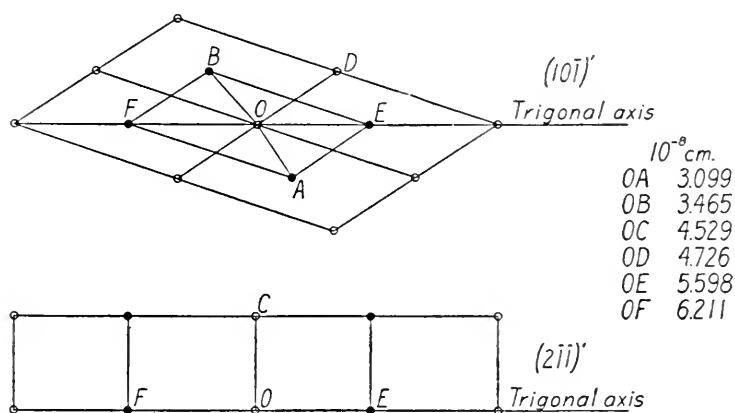


FIG. 2.



by the location of the photographic spots, which tend to fall short rather than to fall beyond the expected positions,<sup>7</sup> than is the relative position of the two lattices by the frequency of occurrence

<sup>7</sup> L. W. McKeehan, JOUR. FRANK. INST., 193, 231-242, Feb., 1922.



of reflection from certain planes. In particular, the appearance of spots attributable to the planes  $(221)'$  and  $(311)'$ , and the absence of any attributable to  $(422)'$ ,  $(330)'$  and  $(411)'$ , suggests that the bismuth atoms are not as uniformly spaced along the trigonal axis as the value  $u = 0.474$  requires. The new data, however, are not of such an accuracy that any estimate can be made of a suitable reduction in the value of  $u$ .

The distances between adjacent atom-centres have been calculated for  $u = 0.474$ , and are given in Fig. 2 which shows the relative positions of the lattice-points on simple planes containing the trigonal axis and therefore common to both lattices. Considering the three planes of each type, the twenty lattice points nearest to any point we may select, lie as follows:

Of the other lattice: 3 at  $3.099 \times 10^{-8}$  cm.  
                               3 at  $3.465 \times 10^{-8}$  cm.  
                               1 at  $5.598 \times 10^{-8}$  cm.  
                               1 at  $6.211 \times 10^{-8}$  cm.  
 Of the same lattice: 6 at  $4.529 \times 10^{-8}$  cm.  
                               6 at  $4.726 \times 10^{-8}$  cm.

If we attempt to dispose of three valence electrons per atom in the most symmetrical and probable way, in the manner recently developed by Thomson,<sup>8</sup> we will find that they may best be put between the closest atom pairs, those separated by less than  $3.5 \times 10^{-8}$  cm. No attempt has been made to calculate the stability or other properties of such an arrangement.

---

**Early References Pertaining to Chemical Warfare** have been collected by C. A. BROWNE (*Jour. Ind. Eng. Chem.*, 1922, xiv, 646). During the Crimean War proposals were made to load incendiary shells with a solution of phosphorus in carbon disulphide and to load gas shells with cacodyl cyanide. During the Napoleonic Wars, an attempt was made to manufacture infernal machines or incendiary bombs containing phosphorus and potassium chlorate. Gunpowder was used by the Arabs and Byzantine Greeks for rockets and fire balls; the Germans applied it for loading fire-arms. Greek fire was probably a mixture of naphtha and quicklime with a certain amount of sulphur and pitch; when this mixture is wet with water, the hydration of the quicklime evolves sufficient heat to ignite the naphtha and other ingredients.

J. S. H.

---

<sup>8</sup> J. J. Thomson, *Phil. Mag.*, (6), 43, 721-757, April, 1922.



# THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.\*

BY

WILLIAM D. HARKINS, Ph.D.

Department of Chemistry, University of Chicago.

## 68. EXPERIMENTS ON THE SEPARATION OF MERCURY INTO ISOTOPES.

THE first isotopic material obtained in appreciable quantities was secured by Harkins and Broeker, who separated chlorine, as announced in February, 1920. Eight months later Broensted and Hevesy announced a separation of a much smaller magnitude, 50 parts per million in density, obtained by evaporating mercury at low pressures. Later they secured a density difference of 490 parts per million, but obtained only very small fractions of 0.2 and 0.3 cubic centimetre. The magnitude of the separation obtained in this laboratory is undoubtedly greater when the large size of the fractions is taken into account. The methods of separation used in this laboratory for mercury are as follows:

Method 1. Diffusion through filter paper at low pressures (Doctor Mulliken).

Method 2. (a) Evaporation at low pressures (Mulliken and Harkins, and Harkins and Madorsky).

(b) Distillation at very low pressures (Mulliken and Harkins).

Method 3. Methods 1 and 2a combined in one operation, but with the diffusion through filter paper as the principal process. Evaporative-diffusion (Doctor Mulliken.)

These three methods will be described in the following sections, but it may be stated that the combination method seems to give the most promise where an extensive separation is desired.

## 69. SEPARATION OF THE ISOTOPES OF MERCURY BY EVAPORATION AT LOW PRESSURES.

Only the purest mercury was used in this work, as is evident from the extensive study described later as made by Doctor Mulliken on the purification of mercury. Fig. 31 shows the design of an extremely efficient apparatus in which the molecules have to travel only about 5 mm. from the liquid surface before they condense on the roof (*R*), which is cooled with liquid air, or with carbon dioxide snow in toluene. Fig. 32 gives a slightly less efficient apparatus in which the use of liquid air

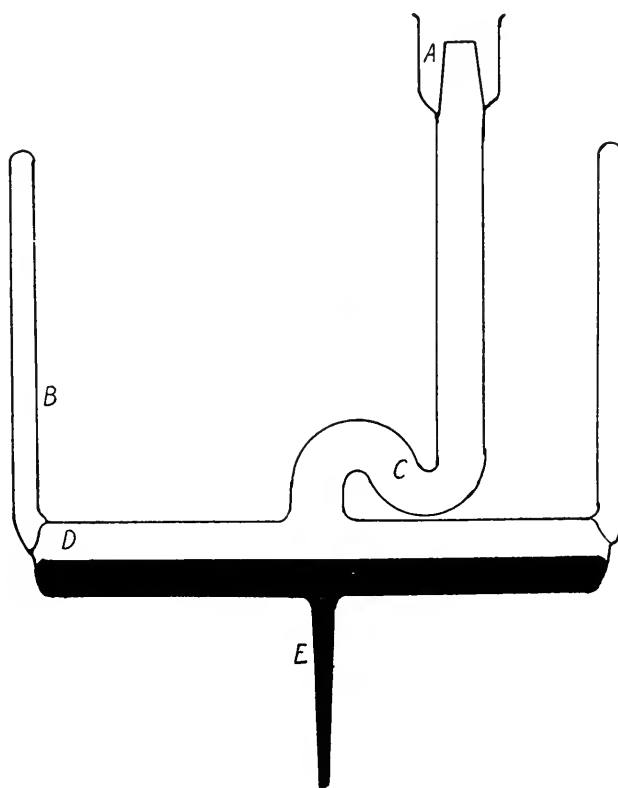
---

\* Concluded from page 814, vol. 194, December, 1922.



is unnecessary, the chamber *C* being filled with ice and water. The molecules which condense on the lower part of the roof *C* gather in drops, and these roll down the roof and collect in the annular catch *D*, since the slope of this roof is made sufficiently steep so that drops of mercury will adhere to it. Thus the

FIG. 31.



Efficient form of evaporator for the separation of mercury into isotopes.

light fraction collects in *E*, while the heavy fraction remains in the chamber *B*.

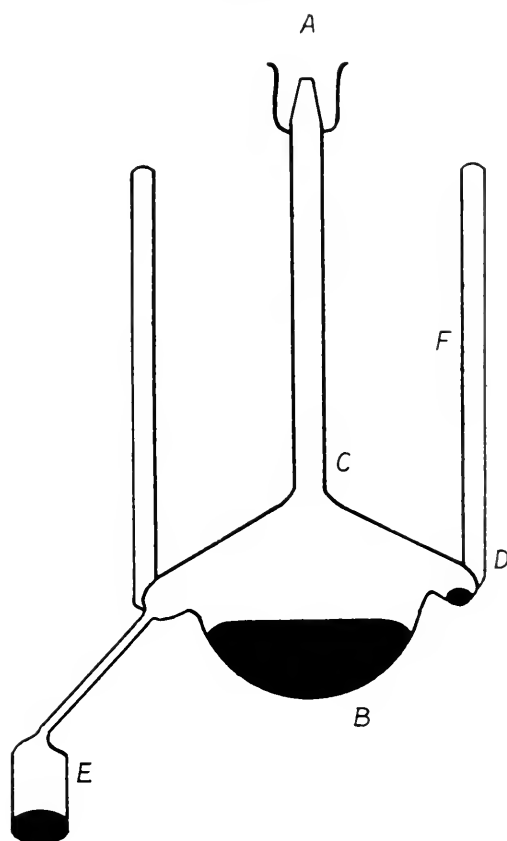
The apparatus was filled through *A* and emptied by cutting off *E*,<sup>92</sup> containing the condensate, and then pouring the residue out through the opening. The ground-glass joint *A* was connected to a mercury diffusion pump and oil pump, and to a McLeod gage. During the runs the apparatus was evacuated to a pressure of  $10^{-4}$  to  $10^{-5}$  mm. The efficiency was probably not much reduced until the pressure rose to about  $10^{-3}$  mm., when the presence of air caused a considerable slowing up of the opera-

<sup>92</sup> If a mercury-sealed stopcock is put at the bottom of *E*, the fractions which collect in *E* can be run out into an evacuated vessel at any time. This has been done in the later work.



tion, and some of the mercury molecules were then deflected so that they condensed on the roof of *D*. A difference in density of 133 parts per million, and in atomic weight of 0.027 unit was obtained very quickly, but no attempt was made to obtain a larger separation in this apparatus, since the work of the laboratory was for a year focussed upon a general survey of the efficiency of various processes of separating isotopes. By the use of this

FIG. 32.



Cross-section of evaporator.

apparatus it was found that the separation coefficient for mercury is equal to 0.0057, but a later careful study by Doctor Mulliken showed that it is more nearly 0.0063, at least for diffusion through filter paper, as it is given in Table XLI.

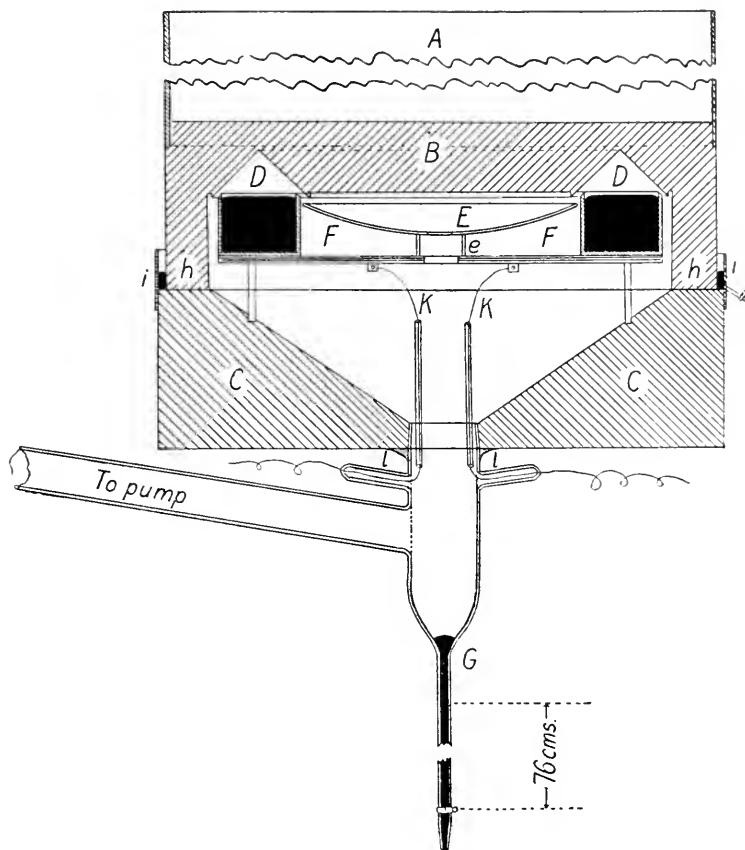
**70. SEPARATION OF THE ISOTOPES OF MERCURY BY EVAPORATION AT LOW PRESSURES IN A LARGE STEEL APPARATUS.**

The apparatus described in the last section, since it is constructed of glass, cannot be made so that it gives a very large mercury surface in a vacuum, so a somewhat similar steel apparatus, which may be built with almost any desired surface, has been



designed by Mr. S. L. Madorsky and the writer. Fig. 33 shows a vertical section of such an apparatus, the trough of which will hold 2600 grams of mercury, while Fig. 34 shows the design of a similar apparatus to hold 11,500 grams. The former apparatus gives an efficiency of about 81 per cent. in terms of Mulliken's coefficient when operated at a rate of 25 c.c. per hour.

FIG. 33.



Steel apparatus for the separation of mercury into isotopes by vaporization. *A*, cylinder for ice; *B*, circular condensing roof, made of steel; *CC*, drain for the light fractions, made of steel; *DD*, annular steel trough holding 190 c.c. of mercury; *E*, watch glass with hole in centre, supported on a short glass tube, *e*; *FF*, heating element made of calorized wire and supported on glass rods; *G*, collecting tube made of glass; *hh*, ground joint; *ii*, mercury seal; *kk*, platinum wires; *ll*, ground joint and sealing wax.

The latter apparatus is in process of construction, so its efficiency has not been tested, but it should be about the same with a rate of evaporation of 50 c.c. per hour, at least at the beginning of the run.

The roof, the base, and the trough of the apparatus were cut from three steel forgings. Cast steel was not used since it is more liable to exhibit leaks and to give off large amounts of gas. The mercury is vaporized from the steel trough *D* while the



pressure of air in the apparatus is kept between 0.0001 and 0.001 mm. pressure. In the smaller apparatus the trough rests upon an iron plate in which is embedded a calorized nichrome resistance wire  $F$ , insulated by magnesium oxide surrounded by an iron sheath. In the larger apparatus the heating wire lies inside the mercury in the trough, but in contact with the bottom of the latter. The supports ( $f$ ) on which the trough rests are made from glass or porcelain rods. The electric current is carried to the heating coil by two heavy platinum wires ( $i$ ) sealed into the walls of the glass tube ( $G$ ),\* which serves to lead to the pump, and to drain off the mercury as it condenses. The platinum wires are insulated by two glass or porcelain tubes ( $l$ ). The glass tube ( $G$ ) is connected with the steel tube ( $S$ ) by a ground, mercury sealed joint, as shown in Fig. 34. The direct connection with the lower steel disc, as shown in Fig. 33, has been abandoned, though it gives good service, since the mercury-sealed joint is easier to detach. The large ground joint ( $h$ ), between the roof and the base of the apparatus, is kept tight by a mercury seal ( $i$ ), the mercury of which is kept in place by a thin steel band. The slope of the roof above  $D$  is  $45^\circ$ , which is sufficiently steep to cause the drops of mercury to slide down the slope, rather than drop back into the trough.

*Operation of the Apparatus.*—The trough of the thoroughly clean apparatus is filled with purest mercury, the roof fitted to the base, the mercury run in around the joint, the vacuum pumps started, and the current turned on the heater. The large chamber  $A$  is at once filled with sufficient ice to last four hours. The lower end of the long glass tube  $G$ , which has been sealed off below the stopcock with a long point, begins to fill with mercury. This has an atomic weight 0.006 unit lower than ordinary mercury, that is the liquid which collects first in the tube has a density 30 parts per million lower than ordinary mercury.

The molecules which escape from the surface of the trough ( $D$ ) travel a distance of only from 1 to 2.5 cm. before they strike the cold roof ( $R$ ), provided the trough is full and that they move vertically upward. While this distance is many times the mean free path of the molecules, the high efficiency obtained (81 per cent.) indicates that not over 19 per cent. of the mole-

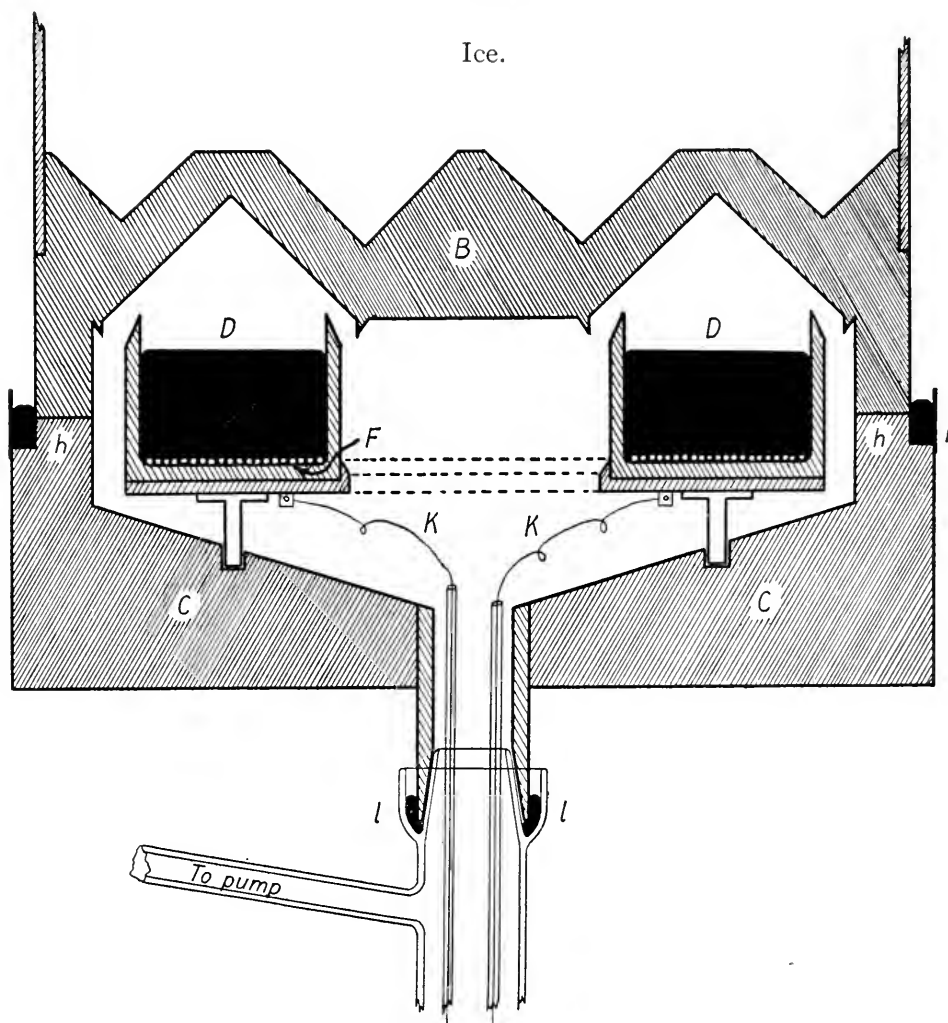
---

\* The apparatus shown in Fig. 34 has now been modified so that these platinum wires pass through insulating plugs in the steel base.



cules return to the evaporating surface. The rapidly moving unidirectional stream of mercury molecules from the hot surface ( $100^{\circ}$  to  $15^{\circ}$  C.) to the cold surface serves to almost entirely prevent such a return. In the larger apparatus a *few* of the molecules must move 3 cm. upward from the full trough before they

FIG. 34.



Large steel apparatus of 850 c.c. capacity for the separation of mercury into isotopes (Harkins).  
The significance of the lettering is the same as given under Fig. 33.

strike the roof. As the evaporation proceeds the distance increases, and this decreases slightly the efficiency toward the end of the run.

Table XLII shows the results obtained in an average run with the smaller apparatus, starting with mercury of the ordinary atomic weight. As soon as it is completed the large apparatus



will be used for all of the work in which ordinary mercury is fractionated.

TABLE XLII.

*Fractionation Scheme for 190 c.c., or 2600 gram Samples of Ordinary Atomic Weight.*

Frac- tion.	Per cent.	C.C.	Weight.	Cut C or C <sub>2</sub> -C <sub>1</sub> .	Change of Density in Parts per Million.			Change of Atomic Weight.	
					90 per cent.	81 per cent.	Actual.	190 per cent.	Actual.
1	20	38	520	1.25	-25.4	-22.9	-22.8	-0.005	-0.0046
2	20	38	520	1.66-1.25	-18.2	-16.4		-0.0036	
3	15	28.5	390	2.22-1.66	-10.2	-9.2		-0.0020	
4	15	28.5	390	3.33-2.22	-0.4	-0.36		-0.00008	
5	10	19	260	5-3.33	+10.9	+9.8		+0.0022	
6	10	19	260	10-5	+26.2	+23.6		+0.0052	
7	5	9.5	130	20-10	+45.9	+41.3		+0.0092	
8	5	9.5	130	20	+85.2	+76.7	+78	+0.017	+0.016

The light fractions thus produced were refractionated as follows:

TABLE XLIII.

*Fractionation Scheme for the Light Fractions of Table XLII.*

Fraction.	Per cent.	Weight.	Cut C or C <sub>2</sub> -C <sub>1</sub> .	Change of Density.			Density Actual.	Atomic Weight.
				90 per cent.	81 per cent.	Actual.		
1	25	650	1.33	-24.7	-22.2	-22.2	-44.4	-0.0089
2	25	650	2-1.33	-14.8	-13.3			
3	25	650	4-2	0	0			
4	25	650	4	+39.5	+39.5			

In each of the two above tables the column headed "Change of Density, 90 per cent.," gives the theoretical values for the separation based upon the separation coefficient .0057, which is the highest separation so far obtained in any evaporation at low pressures. The reason for calling this a 90 per cent. value is that, as stated before, Mulliken has obtained a separation by diffusion through filter paper which is represented by the coefficient 0.0063. Runs VI to VIII were simply repetitions of that listed in Table XLIII. Run IX gave 55 c.c. with  $\Delta = -65.2$ , where  $\Delta$  is the increase in density in parts per million.

Runs X to XII were made on the basis of a 50 per cent. cut. Here the increase and decrease of density should both be 17.7 parts. In the tenth run the 55 c.c. from run IX was split in this way and the theory indicated that the density should be  $\Delta = -(65.2 + 17) = 82.2$ . In the eleventh run this was divided in the same way again, with an estimated  $\Delta = -(82.2 \div 17.7) = 99.9$ , and in the twelfth,  $\Delta = -(99.9 + 15.9) = 115.8$ . The determined value was  $\Delta = -112.4$ , which indicates that the efficiency was high. It should be said that the calculations of this paragraph were made on the basis of 0.0057 as the highest experi-



mental separation coefficient for a vaporization process. The seventh fraction of runs I to V (Table XLII) were combined, which gave 50 c.c. with an estimated  $\Delta$  of +36. This was evaporated into three nearly equal fractions. The last fraction of 17 c.c. was combined with the eighth fractions of runs II to V. This gave 65 c.c. with an estimated  $\Delta$  of +64, which was evaporated down to 12 c.c. with an estimated  $\Delta = +106.5$ , and a determined value of 95.9. This indicates that the last evaporations were less efficient than the others.

The total difference of density obtained in about twenty days of operation of this apparatus was 266 parts per million, or an atomic weight difference of 0.053. The end fractions are quite large, however, and weigh 224 grams for the light, and 272 grams for the heavy fraction. The difference of atomic weight thus far secured is 0.070 unit and a few days of further operation will give a change equal to 0.110 unit.

#### 71. SEPARATION OF THE ISOTOPES OF MERCURY BY DISTILLATION AT LOW PRESSURES.

The interesting fact that even in the ordinary purification of mercury by distillation at low pressures there is an easily measurable separation of the isotopes of mercury, commonly 4 to 7 parts per million increase of density of the residue, was first observed by Mulliken and Harkins.<sup>93</sup> A detailed study of such distillations by Mulliken showed that when the distillation flask has a neck of large diameter the efficiency of such a process may be made as great as 67 per cent. of that given by a completely irreversible evaporation, provided the water condenser is put as close to the flask as is possible; and Laby and Mephram<sup>94</sup> report a result which corresponds to an efficiency of 49 per cent. The most striking results of the investigation in this laboratory<sup>95</sup> are:

(1) Distillation at the rate of 15 c.c., or 204 grams per hour (3.5 gms./cm.<sup>2</sup> hr.), from a 300-c.c. flask with a neck bent over and sealed to a water-jacketed condenser, gave an efficiency of 50 per cent., even when the air pressure was as 0.1 or 0.2 mm. Since the highest efficiency obtained by the evaporation method is only 90 per cent., it is seen that the extremely simple distillation method is a very good one. The efficiencies obtained at different

<sup>93</sup> Mulliken and Harkins: *J. Am. Chem. Soc.*, **44**, 60-62 (Jan., 1922).

<sup>94</sup> Laby and Mephram: *Nature*, **109**, 206 (1922).

<sup>95</sup> Mulliken: *J. Am. Chem. Soc.* (Nov., 1922).



pressures are: 58 per cent. at  $10^{-5}$  mm., 54 per cent. at 0.02 mm., 46 per cent. at 0.8 mm., 20 per cent. at 10 mm., and 9 per cent. at 30 mm.

(2) *A film of material such as soot on the surface of the mercury increases the efficiency* of the separation markedly at moderate or high, but not at low, rates of vaporization. The following examples illustrate the considerable magnitude of this effect, the evaporation rates being given in grams per cm.<sup>2</sup> per hour: (1) without film, efficiency 54 per cent. at 1.5 grams, 27 per cent. at 8 grams, and 24 per cent. at 24 grams; (2) with film, 58 per cent. at 3 grams, 49 per cent. at 14 grams, and 37 per cent. at 36 grams.

## 72. SEPARATION OF THE ISOTOPES OF MERCURY BY THE HIGHLY EFFICIENT AND RAPID METHOD OF EVAPORATIVE-DIFFUSION.

The combination method of evaporative-diffusion, as applied by Mulliken in this laboratory, is by far the most efficient of all of the processes as yet devised for the separation of isotopes. It also has the further great advantages that it requires only tap water for cooling, and that its efficiency is very high at air pressures as great as 0.2 mm., which means that the apparatus operates well with an oil vacuum pump of small size even when the pump is not in specially good order. The apparatus is by far the most rapid in its operation of any thus far tested; also more rapid than any yet devised, with the possible exception of a very large steel apparatus designed by the writer, but not constructed on account of its high cost.

Whereas the highest efficiency obtained by Broensted and Hevesy, or Mulliken and Harkins, by the use of a single evaporation, is 90 per cent. in terms of Mulliken's value of the separation coefficient, 0.0063, the evaporative-diffusion gives efficiencies as high as 120 per cent., and at very high speeds of operation the efficiency is 100 per cent., of which 25 per cent. is contributed by the evaporation, and the rest by the diffusion through filter paper. It can be easily seen that this indicates that the efficiency of the diffusion is *more* than 75 per cent., though this is not apparent without a careful consideration of the factors involved. A battery of six units has been constructed. Each unit consists of a 500-c.c. flask of pyrex glass, fitted with a long vertical tube of filter paper above it, the latter being surrounded by two concentric tubes of pyrex glass. Between these the water used for condensing is



passed. *By the use of the six units mercury can be evaporated with good efficiency at the rate of a ton in twenty-four hours or less.*

With only about four days of operation the three units first constructed gave 20 c.c. of mercury whose atomic weight is 0.030 unit higher, and 150 c.c. 0.016 unit lower than ordinary mercury, a total difference of 0.046 unit. At present 136 c.c. of -121 p.p.m. and 47 c.c. of +203 p.p.m. have been secured, with an atomic weight difference of 0.061 unit. It is obvious that the size of the fractions as well as the atomic weight change should be considered in connection with the degree of separation. If operated at about the present rate of diffusion, 680 grams of mercury vapor per hour per unit at 100 per cent. efficiency, the six units of this apparatus will give a full set of fractions of 680 grams each at intervals of 22 parts per million of density difference (0.0044 unit of atomic weight) with separations between the end fractions as follows: 0.1 unit of atomic weight difference in 86 hours, 0.2 unit in 717 hours, 0.3 unit in 2281 hours, etc. Thus in 228 days of 10 hours each, 47 kilos of mercury could be distributed evenly over a range of 0.3 unit of atomic weight, in the form of 69 fractions of 680 grams of mercury each. It is evident that a considerably greater atomic weight difference could be obtained in the same time by decreasing the size of the fractions.

### 73. DETERMINATION OF THE DENSITY OF MERCURY.

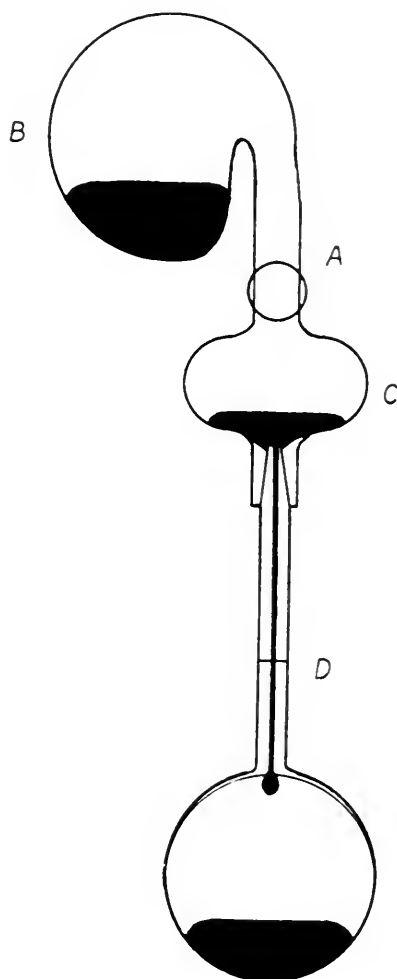
The density of mercury is determined by the use of a special pycnometer,<sup>84</sup> by means of which it is probable that a precision of one part in 5 million can be attained. With very ordinary precautions the variation is about 1 part in 2 million. The pycnometer consists of a glass bulb sealed to a capillary of 0.2 mm. internal diameter (Fig. 35D). This is fitted to a filling device (*BC*) by means of a tight ground-glass joint. The mercury is first poured into the bulb *B*, the empty pycnometer fitted in place, and the apparatus evacuated through the side tube *A* by means of a good oil vacuum pump. The device is then rotated around *A* until it is in such a position that the pycnometer becomes filled. The latter is then detached and put in a bath whose temperature is slightly above 25°, and by an amount which will cause the mercury meniscus to stand almost exactly on the



fine graduation on the stem, when the temperature is reduced exactly to  $25.000^{\circ}$ . The bulb *C* should contain more mercury than will fill the bulb of the pycnometer, in order to prevent any floating scum from entering the latter.

The edges of the tip of the pycnometer should be well rounded off. What is more important is that the inside of the

FIG. 35.



Pycnometer.

bulb shall be *very smooth*, with no projections of any kind, and also very clean when it is first made. The capillary should have a uniform diameter, but if it is to be used in warm weather, a small bulb may be blown in it near the top, in order to prevent an overflow by expansion during the period of weighing.

Corrections for the buoyancy of the air with varying humidity and barometric pressure may be avoided by the well-known



method of using an exactly similar pycnometer filled with mercury, but with a sealed capillary as a counterpoise. In routine work, however, it has been the custom to rest the single pycnometer in a cup of glass, whose weight has been so chosen that it exactly corrects for buoyancy changes. The former method has the advantage of giving a better correction for the weight of the film of moisture deposited on the outer surface of the glass. The following figures give the results of *five different fillings with two different samples as obtained in ordinary routine work* carried out without very special precautions:

	Filling.	Corrected weight of filled pycnometer.
Sample 1.	1	124.09393
	2	124.09398
Sample 2.	1	124.09391
	2	124.09400
	3	124.09397

Here the *maximum* deviation from the mean is 5 parts in 10 million.

#### 74. EXPERIMENTAL WORK ON THE SEPARATION OF ISOTOPES BY LIQUID CENTRIFUGING.

Joly and Poole<sup>96</sup> were able to separate certain liquid alloys into fractions of different densities, but an attempt to apply this method to the separation of the isotopes of lead was unsuccessful. However, the expected separation was of the same order of magnitude as the errors in the density determinations, so the negative result is not surprising. The peripheral velocity in these experiments was  $10^4$  cm./sec. Poole<sup>97</sup> later discussed the possibility of securing a separation with mercury, but concluded that the density change to be expected, 30 parts per million, would be too small to be measured. Actually 1/60 of this density difference could be detected by the method developed in this laboratory, so Mulliken experimented with mercury in a large centrifuge, which, unfortunately, does not have a very high peripheral velocity. A speed of 2300 r.p.m. was attained, with the outer end of the steel tubes which contained the mercury 26.3, and the inner end 7.1 cm. from the axis. Each of the two tubes contained 13 c.c. The calculated separation between the extreme

<sup>96</sup> Joly and Poole: *Phil. Mag.* (6), 39, 372 (1920).

<sup>97</sup> Poole: *Phil. Mag.* (6), 41, 818 (1921).



ends is 8.8 parts per million, but, since the contents were divided into thirds, only two-thirds of this difference should be obtained, or 5.9 p.p.m. The results were conclusively negative to 0.5 part per million in each of two eight-hour runs. The tubes were as perfectly balanced as was possible, but in spite of this there was some vibration at the highest speeds of the centrifuge. It was not difficult to prove that this vibration is a sufficient cause of the failure of the separation, as is evidenced by the fact that when the mercury in the bottom half of the tube was made 12 parts per million heavier than that in the top half, a half-hour run was sufficient to mix the two halves thoroughly *against the effect of the centrifugal force*. That an eight-hour run should be sufficient to give a centrifugal separation if the vibration could be prevented, seemed to be indicated by the fact that when the two halves of the tube were filled with material differing in density by 12 p.p.m. as described above, and the tube was kept still on a concrete pier, the rate of diffusion was sufficiently great to very nearly eliminate the difference of density in eight hours of standing.

Mr. Jenkins and the writer will repeat the attempt to obtain a centrifugal separation. The tubes will be first filled with tightly packed steel balls, or possibly sand, the top screwed on tightly, and the mercury run in through a hole in the top. It is hoped that the presence of the small balls may sufficiently annul the vibration of the liquid to enable the detection of a separation, though it is not improbable that success will not be attained until a centrifuge with a higher speed and a lesser vibration can be obtained. It is probable that a special centrifuge must be constructed if any considerable separation is desired. If speeds of  $10^5$  cm. per second could be obtained without sufficient vibration to affect the result, a separation of 0.48 of a unit of atomic weight could be attained in one operation.

The values of the centrifugal separation coefficients (values for  $P$  in equation 28, section 68) have been calculated by Mulliken with the following results (times  $10^{-12}$  at  $20^\circ$ ): Li, 1.16; B, 1.85; Ne, 7.38; Mg, 8.97; Cl, 14.5; Ni, 18.4; Zn, 53; Br, 20.4, and Hg, 47. For ordinary *air* the coefficient would be about  $62 \times 10^{-12}$ . It will be noted that the coefficients are very favorable to the heavy elements, and this should be particularly true of the elements of even atomic numbers between 30 and



80. A peculiarity of these coefficients, as compared with diffusion coefficients, is that the former are independent of the state of combination of the element, and are thus characteristic of the element, while the latter are inversely proportional to the molecular weight.

75. THEORY OF THE SEPARATION OF ISOTOPES BY NON-EQUILIBRIUM EVAPORATION.<sup>98</sup>

The surface of a liquid may act as a diffusion membrane in which the apertures are of molecular dimensions. Since this represents the simplest type of diffusion membrane the equations for the separation of isotopes by diffusion will be developed from a consideration of this special case. Meyer has shown in a very simple way<sup>99</sup> that the number ( $N$ ) of molecules of a gas at rest which strike 1 square centimetre of the wall of the containing vessel, is given by the following equation:

$$N = \frac{1}{4} nv \quad (A)$$

in which  $n$  is the number of molecules in 1 cubic centimetre of the gas, and  $v$  is the *average* velocity of its molecules.

According to the Maxwell distribution law the probability ( $y$ ) of a velocity whose magnitude is  $x$  is given by the equation

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2} \quad (B)$$

From this equation it may be seen that the relation between the average velocity and the mean velocity ( $c$ ) is

$$v = c \left( \frac{8}{3\pi} \right)^{1/2} \quad (C)$$

so equation (A) becomes

$$N = \frac{1}{4} nc \left( \frac{8}{3\pi} \right)^{1/2} = \frac{1}{\sqrt{6\pi}} nc \quad (A')$$

The kinetic energy of translation of one mol of gas molecules is given by the well-known equation:

$$E = \frac{1}{2} M c^2 = \frac{3}{2} RT \quad (D)$$

so

$$c = \sqrt{\frac{3RT}{M}} \quad (E)$$

<sup>98</sup> This and the following sections on the theory of the separation of isotopes have been taken largely from a paper by Mulliken and Harkins, *J. Am. Chem. Soc.*, **44**, 37-65 (1922).

<sup>99</sup> Meyer: "Kinetic Theory of Gases" (1899), pages 80 to 83.



A combination of equations (A) and (E) gives

$$N = n \left( \frac{RT}{2\pi M} \right)^{1/2} \quad (F)$$

Now  $nM = \rho$ , where  $\rho$  is the density of the gas, and is given by the equation

$$\rho = \frac{M}{V} = \frac{MP}{RT} \quad (G)$$

in which  $M$  is the molecular weight and  $V$  is the molecular volume. So

$$n = \frac{P}{RT} \quad (H)$$

A combination of (F) and (H) gives our fundamental equation

$$N = \frac{P}{\sqrt{2\pi MRT}} \quad (I)$$

Equation (I) gives the number of molecules of a dilute vapor which strike one square centimetre of the surface of a pure liquid in equilibrium with it, and so necessarily the number which evaporate from unit area in unit time. For an ideal solution, such as a mixture of isotopes, the relation  $N_a = \frac{p x_a}{\sqrt{2\pi MRT}}$  should hold for each isotopic component ( $a$ ), if the vapor pressure has the same value ( $p$ ) for each such component when pure. That this is at least very closely true is shown by Aston's failure to obtain any separation of the isotopes of neon by 3000 fractionations, and by other evidence.<sup>100</sup> In an ordinary distillation, the rate of distillation is negligibly small compared with  $N$ , and there is practical equilibrium between liquid and vapor. Although lighter molecules evaporate faster from the liquid, they also return faster from the vapor, so that the two phases have practically the same isotopic composition. If, however, the pressure is made very low, and the condensing surface placed so close to the evaporating surface that practically all the evaporating molecules are condensed, it is clear that the condensate must be enriched in the lighter isotopes. This method of evaporation is really equivalent to molecular effusion.

<sup>100</sup> In view of the thermodynamic relation between vapor pressure and solubility, the failure of Richards and Hall [*J. Am. Chem. Soc.*, **39**, 531 (1917)], to secure any change of atomic weight by 1000 recrystallizations of lead nitrate from radioactive material, is additional evidence for the very close equality of the vapor pressures of isotopes.



The molecules leaving a liquid surface move forward with various velocities and in various directions. The farther a molecule has to travel before reaching a cold surface, the greater is its chance of collision with another molecule; and the greater the number of collisions it suffers, the more likely it is to acquire a backward component of velocity. If there are many collisions per molecule, the condition of a saturated vapor is approached, and the efficiency of the separation is reduced. The presence of air-molecules, which, being non-condensable, and moving in all directions, will increase the number of unfavorable collisions. For maximum efficiency, (1) the apparatus must be thoroughly evacuated, (2) the rate of evaporation must be sufficiently low, and (3) the condensing surface must be as close as possible to the evaporating surface. At least in the case of mercury (which has very heavy atoms), as shown by the present experimental work, the atoms can move through a distance equal to several times the mean free path for the saturated vapor, and can suffer a number of collisions, without much loss of efficiency.

In order that the theoretical efficiency shall be attained, the evaporating liquid must be kept at a uniform composition throughout, by diffusion, convection, or by artificial mixing. Otherwise the accumulation of heavy molecules in the surface will cause a corresponding increase in their proportion in the condensate. Approximate calculations indicate, however, that liquid diffusion alone is capable of preventing more than a slight loss of efficiency, even for fairly considerable rates of evaporation. This is in harmony with the experimental results. Because of the impossibility of rapid mixing, the separation of isotopes by evaporation from a solid surface is evidently impracticable. The range of application of the method may, however, be extended by the use of solvents.

*Comparison of Methods.*—The choice of elements suitable for separation by evaporation is limited to those forming suitable compounds or solutions or themselves existing as liquids having a small vapor pressure at a convenient temperature. To be suitable for a diffusion method, a substance must exist as a gas or have a considerable vapor pressure preferably at room temperature. The diffusion method probably has wider applicability than the evaporation method.



# 76. DEVELOPMENT OF EQUATIONS SHOWING RATE OF CHANGE OF COMPOSITION AND ATOMIC WEIGHT IN DIFFUSION PROCESSES.

## Notation.

(Letters preceded by a  $(*)$  in the following list are always used with one of the subscripts 1, 2, -- $a$ -- $b$ -- $s$ -- $n$ , each of which is used to refer to a particular molecular species;  $a$  and  $b$  refer to *any* molecular species,  $s$  and  $n$  to the last of a set or series. Letters preceded by a  $(+)$  may be used with the subscript  $0$  to denote initial values of the quantities to which they refer, for example,  $N_0$ ,  $(N_1)_0$ ,  $(x_a)_0$ .

$(*)N$  = rate of flow in mols per sec.

$(+)N$  = total number of mols of material in *residue* at any time during a diffusion

$(*+)N$  = number of mols of an individual component in the *residue*

$(*+).x$  = mol-fraction

$(*)x$  = increase in mol-fraction of a component over its initial value, in the residue;  $(*)\Delta^c x$ , in the *total condensate*;  $(*)\Delta^{ic} x$ , in the *instantaneous condensate*

$M$  = ordinary (average) molecular weight

$(*)M$  = molecular weight of a particular isotope  
 $\Delta M$ ,  $\Delta^c M$ ,  $\Delta^{ic} M$ , increase in molecular weight of residue, total condensate, and instantaneous condensate, respectively

$k_a^1$  =  $c\sqrt{M_1/M_a}$ , where  $c$  is between 2 and 1; for example  
 $k_3^1 = c\sqrt{M_1/M_3}$

$k_1^1$  =  $c\sqrt{M_1/M_1} = 1$

$R$  = gas constant

$T$  = absolute temperature

$(*)p$  = saturated vapor pressure (or, gaseous pressure in general)

$r$  = radius of capillary tube;  $l$  = length of same

$(*)\lambda$  = mean free path of gas molecules

$(*)c$  = mean velocity of gas molecules

$(*)n$  = number of mols. or molecules, per c.c.

$(*)\frac{\delta n}{\delta z}$  = concentration gradient

$(*)d_{1s}$ ,  $d_{2s}$ , etc. = distance between centres of molecules 1 and  $s$ , or 2 and  $s$ , respectively, at impact; for example  $d_{12}$ ,  $d_{21}$ . Note that  $d_{11}$  or  $d_{12}$  become  $d_1$  and  $d_2$

$A$ ,  $A'$ ,  $B$ ,  $B'$  = (see Equations 5, 5', 7 and 7')

$C = N_0/N$  = "cut"

$D$ ,  $D'$ ,  $E$ ,  $E'$  = (see Equations 6A, 6A', 7A, 7A')

$S$  =  $\Sigma(x_a k_a^1) = x_1 + x_2 k_2^1 + \dots + x_n k_n^1$

$n_c$  = number of atoms of an isotopic element in a compound, *c.g.*,  
 for  $\text{CCl}_4$ ,  $n_c = 4$

*Change in Composition of Residue for the Case of Two Isotopes.*—For a mixture of two isotopes having molecular



weights  $M_1$  and  $M_2$ , and mol-fractions  $x_1$  and  $x_2$ , the relative rate of molecular diffusion, molecular effusion, or evaporation, is given by

$$-dN_2/-dN_1 = (x_2/\sqrt{M_2}) (\sqrt{M_1}/x_1) = (x_2/x_1) \sqrt{M_1/M_2} = k_2^1 (x_2/x_1). \quad (1)$$

$N_1$  and  $N_2$  denote the respective numbers of mols of the two isotopes in the *residue* at any time.  $N$  will be used to denote  $N_1 + N_2$ , and  $N_0$  to denote the number of mols initially present. For gaseous diffusion, the relation is the same, except that  $k_2^1$  means  $c\sqrt{M_1/M_2}$ , where  $c$  is some number between 1 and 2. Rearranging Equation 1 and noting that  $N_1 = N.x_1$  and  $N_2 = N.x_2$

$$dN_2/x_2 = k_2^1 dN_1/x_1 \text{ or } \frac{Nd x_2 + x_2 dN}{x_2} = k_2^1 \left( \frac{Nd x_1 + x_1 dN}{x_1} \right).$$

$$\text{Then,} \quad (1-k) dN/N = k \left( \frac{dx_1}{x_1} \right) - \frac{dx_2}{x_2}. \quad (2)$$

Integrating,

$$(1-k) \ln N/N_0 = k \ln (x_1/(x_1)_0) - \ln (x_2/(x_2)_0).$$

Or, denoting  $N_0/N$ , the "cut," by  $C$ ,

$$(1-k) \log C = k (\log(x_1)_0 - \log x_1) - \log (x_2)_0 + \log x_2. \quad (3)$$

This equation can be used to calculate the cut necessary to obtain any desired change in the composition of the residue, the initial composition being known. The change in atomic weight of the residue for a given change in composition may be obtained from the relation,  $\Delta M = (M_2 - M_1) \Delta x_2$ .<sup>101</sup> For the diffusate, the change,  $\Delta' M$ , is exactly  $-\Delta M / (C - 1)$  (see Equation 14, p. 90). In connection with his work on the separation of the rare gases, Rayleigh<sup>102</sup> developed a less direct but simpler equation, which is rather more convenient for calculation than Equation 3. He uses the term enrichment ratio, symbolized by  $r$ , for  $\frac{x_2/(x_2)_0}{x_1/(x_1)_0}$ .

Using the symbols of the present section, Rayleigh's relation can be reduced<sup>103</sup> to

$$C = [x_1/(x_1)_0] \cdot r^{1/1-k} \quad (4)$$

<sup>101</sup> In general, for a mixture of ( $n$ ) isotopes, if the atomic or molecular volumes are equal, as the work of Richards and Wadsworth [*J. Am. Chem. Soc.*, **38**, 221 (1916)] shows to be true in the case of the atomic volume of solid lead,  $\Delta M = (M_2 - M_1) \Delta x_2 + (M_3 - M_1) \Delta x_3 + \dots (M_n - M_1) \Delta x_n = \Sigma (M_a - M_1) \Delta x_a$ . This relation applies to mixtures of isotopic atoms or of isotopic molecules, *i. e.*, molecules differing only in containing atoms which are isotopes of each other, *e. g.*,  $\text{HCl}_{35}$  and  $\text{HCl}_{37}$ ;  $\text{CH}_2(\text{Cl}_{35})_2$ ,  $\text{CH}_2\text{Cl}_{35}\text{Cl}_{37}$ , and  $\text{CH}_2(\text{Cl}_{37})_2$ ;  $\text{Mg}_{24}\text{O}$ ,  $\text{Mg}_{25}\text{O}$ , and  $\text{Mg}_{26}\text{O}$ .

<sup>102</sup> Rayleigh: *Phil. Mag.*, [5] **42**, 493 (1896).

<sup>103</sup> See Sections 65 and 66.



This is readily obtained from (3). If  $r$  is near unity, Equation 4 becomes, very nearly,  $C = r^{1/(1-k)}$ . In making calculations of  $C$  in terms of  $\Delta M$  or  $\Delta x$ , the easiest method is to calculate  $1/(1-k)$  (compare Table XLI) once for all for the compound under consideration, then to calculate the value of  $r$  corresponding to the assumed value of  $\Delta M$  or  $\Delta x$ , and finally to apply Equation 4.  $\Delta' M$ , the decrease of atomic weight for the *diffusate*, equals  $-\frac{\Delta M}{C-1}$ .

*Simple Equations for Change of Composition of Residue for Small Cuts.*—The use of the exact relations (3) and (4) involves much calculation. For small cuts, or approximate calculations with larger cuts, a very simple relation, which shows clearly the factors governing the rate of separation, can be derived from Equation 2. Noting that  $dx_1 = -dx_2$ , Equation 2 becomes  $(1-k) dN/N = (-k/x_1) dx_2 - dx_2/x_2$ . Noting that  $-dN/N = -\frac{d(N/N_0)}{N/N_0} = d \ln C$ , this reduces to

$$dx_2 = -dx_1 = \frac{(1-k)x_1x_2}{x_1+kx_2} d \ln C = A d \ln C. \quad (5)$$

This quantity  $A$  is really the slope, at the point  $(x_2, \ln C)$ , of the curve obtained by plotting  $x_2$  (or  $-x_1$ ) against  $\ln C$ , starting with  $C = 1$  for  $x_1 = (x_1)_0$  and  $x_2 = (x_2)_0$ . As the composition changes only very slowly with the cut,  $A$  is nearly a constant, so that

$$\Delta x_2 = \frac{(1-k)x_1x_2}{x_1+kx_2} \ln C, \text{ nearly.} \quad (6)$$

By taking average values of  $x_1$  and  $x_2$  this equation will hold rather closely even for a large cut. For the change in atomic weight of the residue,

$$\Delta M = (M_2 - M_1) \Delta x_2 = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1 + kx_2} \ln C = B \ln C. \quad (7)$$

Note that  $C$  is strictly a ratio of mols, or of volumes. Unless  $C$  is extremely large, however, it may without much error be considered a ratio of masses. From Equations 6 and 7 it is seen that the increase in the mol-fraction of heavy isotope and in the atomic weight of the residue proceed arithmetically as the quantity of the latter diminishes exponentially.

*Relation of Rate of Separation to Composition of an Isotopic Mixture.*—The rate at which  $A$  and  $B$  change with the composition or atomic weight of the residue during a diffusion or evapora-



tion can be obtained to a close approximation as follows. Since  $x_1 + kx_2$  is always nearly unity, we can write

$$A = \left( \frac{1-k}{x_1+kx_2} \right), \quad x_1x_2 = Fx_1x_2, \text{ and } B = \frac{1-k}{x_1+kx_2} (M_2-M_1)x_1x_2 = Gx_1x_2,$$

$F$  and  $G$  being regarded as essentially constant. Then

$$\frac{dA}{dx_2} \left( = \frac{dB}{dM} \right) = F \frac{d(x_1x_2)}{dx_2} = F \frac{d(x_2-x_2^2)}{dx_2} = F(1-2x_2) = F(x_1-x_2) = \frac{A(x_1-x_2)}{x_1x_2}. \quad (8)$$

If values of  $A$  or  $B$  are plotted as ordinates against values of  $x_2$  (or  $-x_1$ ) as abscissas, a *portion of a parabola is obtained*, corresponding to the equation  $A = Fx_1x_2 = F(x_2 - x_2^2)$ , or  $B = G(x_2 - x_2^2)$ . This begins at the point ( $x_2 = 0$ ,  $A$  or  $B = 0$ ), rises to a maximum at ( $x_2 = 0.50$ ,  $A = 0.25F$  or  $B = 0.25G$ ), and falls again to ( $x_2 = 1$ ,  $A$  or  $B = 0$ ). Thus *the most favorable mixture for the separation of two given isotopes is that for which  $x_1 = x_2 = 0.50$* . Between  $x_2 = 0.25$  and  $x_2 = 0.75$  the value of  $B$  is still nearly as favorable, but if  $x_2$  falls below 0.05 or 0.10, or rises above 0.90 or 0.95, the rate of separation is much reduced. If  $x_2$  (or  $M$ ) is plotted against  $\ln C$  for the residue, the slope  $A$  (or  $B$ ) of this curve thus approaches zero, and *the curve itself approaches asymptotically the line  $x_2 = 1$  (or  $M = M_2$ )*, as  $\ln C$  continues to increase;<sup>104</sup> the curve is terminated abruptly in the other direction at  $C = 1$ .

The slope  $dA/dx_2$  of the  $A$  parabola is given by Equation 8. Since  $B = (M_2 - M_1) A$ , and  $\Delta M = (M_2 - M_1) \Delta x_2$ , it is evident that  $dB/dM$  is equal to  $dA/dx_2$ . From Equation 8, then,  $dB/dM$  is zero when  $x_2 = 0.50$ , has a maximum positive value when  $x_2 = 0$ , and a maximum negative value when  $x_2 = 1$ . Thus  $B$  (and  $A$ ) increase for the residue (and decrease for the diffusate), during a separation, if  $x_2$  is less than  $x_1$ ; and *vice versa*.

*Modifications of Simple Equations for Large Cuts.*—The quantity  $\frac{dB/B}{dM}$  is useful as a measure of the error in  $B$  when  $\Delta M$  is large.

$$\frac{dB/B}{dM} = \frac{F(x_1-x_2)}{B} = \frac{x_1-x_2}{x_1x_2(M_2-M_1)}.$$

Call this last quantity  $2H$ . For a moderately large change  $\Delta M$  of atomic weight we have, approximately,

<sup>104</sup> See Fig. 36, particularly the curve for lithium.



$$\Delta M = \left[ B + \frac{1}{2} \left( \frac{dB}{dM} \right) \Delta M \right] \ln C = B \left[ 1 + \frac{1}{2} \left( \frac{dB/B}{dM} \right) \Delta M \right] \ln C = B (1 + H \Delta M) \ln C. \quad (9) \quad 108$$

For the case that  $M_2 - M_1 = 2$ , if  $x_2 = 0.01$ , the value of  $H$  is 24.8; if  $x_2 = 0.10$ ,  $H = 2.22$ ; if  $x_2 = 0.25$ ,  $H = 0.67$ ; if  $x_2 = 0.50$ ,  $H = 0$ ; if  $x_2 = 0.75$ ,  $H = -0.67$ , etc. The correction term  $H\Delta M$  is evidently not large unless  $\Delta M$  is considerable, or  $x_2$  is near zero or unity. For ordinary hydrogen chloride,  $x_2 = 0.23$ ,  $B = 0.00950$ , and  $H = +0.76$ . Without using the correction term, we have, for  $\Delta M = 0.05$ ,  $\Delta M = 0.05 = 0.00950 \ln C$ . By putting in the correction term,  $\Delta M = 0.05 = 0.00950 (1.038) \ln C$ . The value of  $C$  calculated from the former expression (Equation 7) is 192.7; that from the latter (Equation 9) is 158.9. The *correct* value of  $C$ , calculated by means of Equation 4, is 159.8. For  $\Delta M = 0.10$ , the respective values of  $C$  obtained by the three methods are 37,140; 17,630; and 18,530. The discrepancies between the results of Equation 4 and Equation 7 are not large, especially from the point of view of the change of atomic weight secured by a given cut, and are in fact much less than would normally result between theory and practice due to unavoidable inefficiency of operation. Equation 9 evidently gives a very close approximation of the results of the exact Equation 4, and is much simpler than the latter, once the values of  $B$  and  $H$  have been calculated for the compound under consideration. Values of  $B$  are given in Table XLI. Equation 10, which likewise gives a very close approximation, is useful for calculating  $\Delta M$  if  $C$  is given.

*Useful Approximate Forms of Simple Equations; Relation of Rate of Separation to Molecular Weights of Isotopes.*—The term  $(1 - k)$  in Equations 6 and 7 can be calculated very quickly and accurately by means of the approximate empirical relation  $(1 - k) = (4/c) (M_2 - M_1) / (3M_2 + M_1)$ . This is correct to within about 0.1 per cent. for the lightest elements, and is *still more exact* for the heavier elements. For example, the exact value of  $1 - k$ , for  $c = 2$ , and  $M_1 = 6$  and  $M_2 = 7$ , is 0.074180, while that calculated from the above relation is 0.074074, or 0.14 per cent. too low. For  $M_1 = 36$ ,  $M_2 = 38$ , the exact value of  $1 - k$  is 0.026672, and the approximate value 0.026667; the latter is only 0.018 per cent. low. Using the relation just given, Equation 6 becomes

<sup>106</sup> Since  $\Delta M = B \ln C$ , nearly, this can also be written,

$$\Delta M = B(1 + BH \ln C) \ln C. \quad (10)$$



$$\Delta x_2 = \frac{(M_2 - M_1)x_1x_2}{(c/4)(3M_2 + M_1)(1 - (1 - k)x_2)} \ln C = A \ln C \text{ (practically)}. \quad (6B)$$

and Equation 7 becomes

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{(c/4)(3M_2 + M_1)(1 - (1 - k)x_2)} \ln C = B \ln C \text{ (practically)}. \quad (7B)$$

$A$  and  $B$  can be calculated with sufficient accuracy in accordance with these equations, the term  $(1 - (1 - k)x_2)$  being readily calculated by the help of the relation given. This term can be neglected entirely for neon and heavier elements, when an accuracy of 1 per cent. is sufficient, giving simplified forms of Equations 6B and 7B which may be called Equations 6BB and 7BB. These can be still further simplified to <sup>106</sup> the still less exact forms,

---


$$\begin{aligned} {}^{106} (1 - k) &= 1 - \frac{c}{\sqrt{M_1/M_2}} = 1 - \frac{c}{\sqrt{1 - (M_2 - M_1)/M_2}} = 1 - \frac{c}{\sqrt{1 - c(M_2 - M_1)/cM_2}} \\ &= 1 - \frac{c}{\sqrt{[1 - (M_2 - M_1)/cM_2]c}} \text{ (nearly)} = 1 - [1 - (M_2 - M_1)/cM_2] \text{ (nearly)} \\ &= (M_2 - M_1)/cM_2 \text{ (nearly)}. \end{aligned}$$

The usual case is  $c = 2$ , but the relation holds for any value of  $c$  (it is of course exact for  $c = 1$ ), provided  $M_2 - M_1$  is small compared with  $M_2$ . The empirical relation  $(1 - k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$  holds very closely even when  $M_2 - M_1$  approaches  $M_2$  in magnitude. This relation reduces to  $2(M_2 - M_1)/(3M_2 + M_1)$  for  $c = 2$ . This can be used for calculating  $B$  of Equation 7.

The quantity  $(1 - k)$  is closely related to the "diffusion exponents" ( $k$ ) and ( $k'$ ) of Harkins and Hayes. ( $k$ ) is equal to  $-1/(1 - k)$ , and ( $k'$ ) to  $-1/(1 - (1/k)) = +k/(1 - k)$ . The "diffusion exponent" is the same (except for the sign) as the exponent of  $r$  in Equation 4 of this section. The rule of Harkins and Hayes that  $\frac{(k) + (k')}{2} = (M_1 + M_2)/(M_1 - M_2)$ , ( $k$ ) and ( $k'$ ) being respectively 0.50 unit greater, or less, than  $(M_1 + M_2)/(M_1 - M_2)$ , agrees with the above empirical relation for  $1 - k$ . [The relation  $(k) - (k') = 1$  is an exact and necessary one, for  $(k) = c\sqrt{M_1}/(c\sqrt{M_1} - c\sqrt{M_2})$ , and  $(k') = \frac{c}{\sqrt{M_2}}/(\frac{c}{\sqrt{M_1}} - \frac{c}{\sqrt{M_2}})$ . The approximations  $(1 - k) = (M_2 - M_1)/cM_2$  [1], and the analogous  $(1 - 1/k) = (M_1 - M_2)/cM_1$  [2], are less exact than the approximations  $(1 - k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$  [3], and  $(1 - 1/k) = (4/c) (M_1 - M_2)/(3M_1 + M_2)$  [4]. For, using [1] and [2], while  $\frac{(k) + (k')}{2} = (-\frac{1}{2})[(1/(1 - k)) + 1/(1 - (1/k))]$   $= \frac{M_1 + M_2}{M_1 - M_2}$ , comes out as it should, the result  $(k) - (k') = 2$  is obviously wrong. Using Equations [3] and [4] for  $(1 - k)$  and  $(1 - (1/k))$ ,  $(k) + (k') = (M_1 + M_2)/(M_1 - M_2)$ , and  $(k) - (k') = 1$ , as it should. The relation of Equation 3, and the corresponding relations,  $(k) = (3M_2 + M_1)c/4(M_1 - M_2)$ , and  $(k') = (3M_1 + M_2)c/4(M_1 - M_2)$ , prove to be so nearly exact that they can be used for calculations by the exact Equation 4.



$$\Delta x_2 = [(M_2 - M_1)x_1x_2/cM_2] \ln C = D \ln C \quad (6A)$$

and

$$\Delta M = [(M_2 - M_1)^2 x_1x_2/cM_2] \ln C = E \ln C \quad (7A)$$

This form of Equation 7 brings out the dependence of the "separation coefficient"  $B$  on the total molecular weight and on the interval between the molecular weights of the two isotopes. For calculations of the separation coefficient, Equation 7B is practically as exact as Equation 7; and Equation 7BB gives results which are very little in error, except for the lightest elements. The very simple approximation given by Equation 7A gives results at worst 3 per cent. low, for elements above neon, but in general Equation 7B or 7BB should be used.

*Change of Composition for Diffusate.*<sup>107</sup>—While the residue is being enriched in the heavier isotopes, the diffusate or condensate is being enriched in the lighter isotopes. For the "instantaneous" diffusate or condensate coming from material of a given composition ( $x_1, x_2$ ) we can write

$$(x_1)^{ic} \frac{dN_1}{dN_1 + dN_2} = \frac{x_1/c\sqrt{M_1}}{x_1/c\sqrt{M_1} + x_2/c\sqrt{M_2}}.$$

From this can be obtained<sup>108</sup> the exact equations

$$(\Delta^{ic}x_1) = \frac{(1-k)x_1x_2}{x_1+kx_2} = +A \quad (11)$$

and

$$\Delta^{ic}M = -(\Delta^{ic}x_1) (M_2 - M_1) = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1+kx_2} = -B \quad (12)$$

The composition of the instantaneous diffusate or condensate always keeps pace with that of the residue,  $x_1^{ic}$ , being just  $A$  units ahead of  $x_1$ , and  $M^{ic}$  just  $B$  units behind  $M$  (see Fig. 30). The composition of the total diffusate is an average of a series of

<sup>107</sup> This is not given by the equations of Rayleigh.

<sup>108</sup>

$$\frac{x_1/c\sqrt{M_1}}{x_1/c\sqrt{M_1} + x_2/c\sqrt{M_2}} = \frac{x_1^c\sqrt{M_2}}{x_1^c\sqrt{M_2} + x_2^c\sqrt{M_1}} = \frac{x_1}{x_1 + kx_2}$$

Then

$$\begin{aligned} x_1^{ic} - x_1 &= \Delta^{ic}x_1 = \frac{x_1}{x_1 + kx_2} - x_1 = \frac{x_1 - x_1^2 - kx_1x_2}{x_1 + kx_2} = \\ &= \frac{x_1 - x_1^2 - kx_1(1 - x_1)}{x_1 + kx_2} = \frac{(1-k)x_1x_2}{x_1 + kx_2} \end{aligned}$$



continuously changing instantaneous diffusates. It obviously approaches that of the original material as the *quantity* of residue approaches the vanishing point. For a mixture of two or any number of isotopes the mol-fraction  $x_a$  of *any* component ( $a$ ) in the total diffusate is necessarily

$$x_a^c = \frac{(N_a)_o - N_a}{N_o - N} = \frac{(x_a)_o N_o - x_a N}{N_o - N} = \frac{(x_a)_o C - x_a}{C - 1};$$

and

$$x_a^c - (x_a)_o = \Delta^c x_a = \frac{(x_a)_o C - x_a}{C - 1} - (x_a)_o = \frac{(x_a)_o - x_a}{C - 1} = \frac{-\Delta x_a}{C - 1} \quad (13)$$

where  $\Delta^c$ ,  $x_a^c$ , etc., refer to the diffusate,  $x_a$ ,  $\Delta$ , etc., to the residue. Correspondingly,

$$\Delta^c M = \Sigma(M_a - M_1) (\Delta^c x_a) = \frac{\Sigma(M_a - M_1) (-\Delta x_a)}{C - 1} = \frac{-\Delta M}{C - 1}. \quad (14)$$

Equations 13 and 14 must hold independently of the nature or efficiency of the diffusion process, and depend only on the assumption that isotopes have equal atomic or molecular volume. By means of these relations, for a 100 per cent. efficient process, we have at once,

$$\Delta^c x_a = -A \frac{\ln C}{C - 1} \quad (15)$$

and

$$\Delta^c M = -B \frac{\ln C}{C - 1}, \quad (16)$$

and corresponding approximate relations with  $D$  and  $E$ . By putting  $C = 1$  and noting that the limit of  $\ln C / (C - 1)$  is unity, as  $C$  approaches unity, Equations 13 and 14 reduce to 11 and 12. For the result of  $n$  successive identical operations on the light fraction, equations analogous to 9 and 10 can be written, *viz.*,

$$\Delta^c M = -nB (1 + H\Delta^c M) \ln C / (C - 1), \quad (17)$$

and

$$\Delta^c M = -nB [1 - BH \ln C / (C - 1)] \ln C / (C - 1), \quad (18)$$

where  $C$  is the cut in *each operation*.

*Effect of Back Pressure on Efficiency.*—In molecular diffusion and molecular effusion, the fractional loss of efficiency due to back pressure is equal to the ratio of the back pressure to the initial pressure. This is shown by the following considerations. The *actual* increase,  $\overline{\Delta x}$ , in the mol-fraction of any isotope in the



diffusate, may be considered as the net result of two processes, forward and backward diffusion, which can be treated as independent (see earlier discussion). Letting  $\Delta x$  denote the increase for a 100 per cent. efficient process, and  $N_1$  and  $N_2$  the quantities of material which diffuse forward and backward, respectively, we can write with a slight approximation,

$$\overline{\Delta x} = \frac{N_1 \overline{\Delta x} - N_2 (\overline{\Delta x} + \Delta x)}{N_1 - N_2}.$$

Simplifying,

$$\overline{\Delta x} = \left( \frac{N_1 - N_2}{N_1} \right) \Delta x = \left( \frac{p_1 - p_2}{p_1} \right) \Delta x.$$

The efficiency of the process is  $\overline{\Delta x} / \Delta x$ , and is thus equal to  $\frac{p_1 - p_2}{p_1}$ ; and the loss of efficiency is  $p_2 / p_1$ . Analogous considerations apply to non-equilibrium evaporation, if  $p_1$  and  $p_2$  now stand for rate of evaporation and rate of return of molecules, respectively. With gaseous diffusion the case is more complicated, but analogous effects are to be expected.

#### 77. GENERAL RELATIONS FOR ANY NUMBER OF ISOTOPES.

For the general case of a mixture of  $n$  isotopes, exact and approximate slope equations analogous to (5), (6), and (7) can be obtained in the following way.  $N$  separate equations of the form of Equation 1 can be written, *viz.*,

$$dN_a / x_a = k_a^1 dN_1 / x_1 \quad (1')$$

and correspondingly,  $n$  equations of the form of Equation 2, *viz.*,

$$(1 - k_a^1) dN / N = k_a^1 dx_1 / x_1 - dx_a / x_a. \quad (2')$$

The equation for which  $a = 1$  is included for the sake of generality in the subsequent development. It is convenient to write all the equations in terms of the lightest component, (1), although any other component could have been chosen. From the  $a^{\text{th}}$  equation of the form of (2), one can get  $dx_a = k_a^1 (x_a / x_1) dx_1 - x_a (1 - k_a^1) dN / N$ . Now it is evident that  $dx = 0$ . Then

$$\Sigma dx_a = \Sigma [k_a^1 (x_a / x_1) dx_1 - (1 - k_a^1) x_a dN / N] = 0.$$

Or

$$(dN / N) \Sigma (x_a - x_a k_a^1) = (dx_1 / x_1) \Sigma x_a k_a^1.$$

Or

$$(dN / N) (1 - \Sigma x_a k_a^1) = (dx_1 / x_1) \Sigma x_a k_a^1.$$

Denoting  $\Sigma x_a k_a^1$  by  $S$ , this becomes  $\frac{1-S}{S} \cdot \frac{dN}{N} = dx_1 / x_1$ . By sub-



stituting the value  $dx_1/x_1 = (1/k^1_a) [(1 - k^1_a) dN/N + dx_a/x_a]$ , obtained from equation (2'), and simplifying, the general expression for any isotope ( $a$ ),

$$dx_a = \frac{x_a(k^1_a - S)}{S} \cdot dN/N = \frac{x_a(S - k^1_a)}{S} \cdot d \ln C = A'_a d \ln C, \quad (5')$$

is obtained. This is the general form of the slope Equation 5, and can be treated like the latter. Thus

$$\Delta x_a = \frac{x_a(S - k^1_a)}{S} \ln C, \text{ nearly.} \quad (6')$$

Since  $\Delta M = \sum [(M_a - M_1) \Delta x_a]$ ,

$$\Delta M = \frac{\sum [(M_a - M_1) x_a (S - k^1_a)]}{S} \cdot \ln C = B' \ln C, \text{ nearly.} \quad (7')$$

This summation has  $n$  terms. It can be shown<sup>109</sup> that the following relation also holds approximately

$$\Delta M = \frac{\sum x_a x_b (M_a - M_b)^2}{c M} \cdot \ln C = E' \ln C \quad (7A')$$

where  $a$  and  $b$  take independently every value from 1 to  $n$ , like terms, however, being taken only once. This summation has  $\frac{n(n-1)}{2}$  different terms. *The calculation of  $E'$  is simpler than that of  $B'$  if  $n$  is not too large; and  $E'$  usually approximates  $B'$*

<sup>109</sup> Since  $1 = \sum x$ , we can write  $S - k^1_a = (x_1 k^1_1 + x_2 k^1_2 + \dots + x_n k^1_n) - (x_1 + x_2 + \dots + x_n) k^1_a = x_1(k^1_1 - k^1_a) + x_2(k^1_2 - k^1_a) + \dots + x_n(k^1_n - k^1_a)$ . In general  $k^1_b - k^1_a = (1 - k^1_a) - (1 - k^1_b) = (M_a - M_1)/cM_a - (M_b - M_1)/cM_b$ , nearly (see note on earlier page),  $= (M_1/c) (M_a - M_b)/M_a M_b$ . Applying this relation to the expression for  $S - k^1_a$ , the latter becomes  $(M_1/c) (1/M_a) \sum [x_b (M_a - M_b)/M_b]$ , where the subscript  $b$ , like  $a$ , stands for all numbers from 1 to  $n$ , to be chose, however, independently of the series of values for  $a$ . By application of this relation, Equation 5 can be written approximately,  $dx_a = (x_a/c) \sum [x_b (M_a - M_b) M_b] \cdot d \ln C$  (5A'), since  $S$  is very nearly unity.

The summation in Equation 7' can be simplified as follows:  $\sum (M_a - M_1) \cdot x_a (S - k^1_a) = S \sum M_a x_a - \sum M_a x_a k^1_a - M_1 S \sum x_a + M_1 \sum x_a k^1_a = S \sum M_a x_a - \sum M_a x_a k^1_a - S M_1 + M_1 S = \sum (M_a x_a) (S - k^1_a)$ . Equation 7' then becomes  $\Delta M = \frac{\ln C}{S} \sum (M_a x_a) (S - k^1_a)$ . Applying the relation already obtained for  $S - K^1_a$ ,

$$\Delta M = [M_1 \ln C / c S] \cdot \sum ([M_a x_a (1/M_a)] \sum [x_b (M_a - M_b) / M_b]).$$

This readily reduces to  $\Delta M = (M_1/c) \frac{(\ln C)}{S} \cdot \sum (x_a x_b (M_a - M_b)^2 / M_a M_b)$ .

This gives the closely approximate relation

$$\Delta M = \frac{\ln C}{c M} \cdot \sum [x_a x_b (M_a - M_b)^2] \cdot \quad (7A')$$



very closely (see table of separation coefficients). The equations for the condensate are very easily generalized. Equations 11 and 12 become

$$\Delta^{\text{ic}}x_a = -A'_a \quad (11')$$

and

$$\Delta^{\text{ic}}M = -B'. \quad (12')$$

Equation 13 holds as it stands for any isotope  $a$ , and Equation 14 for the case of  $n$  isotopes; Equations 15 and 16 become

$$\Delta^{\text{c}}x_a = -A'_a \frac{\ln C}{C-1} \quad (15')$$

and

$$\Delta^{\text{c}}M = -B' \cdot \frac{\ln C}{C-1}. \quad (16')$$

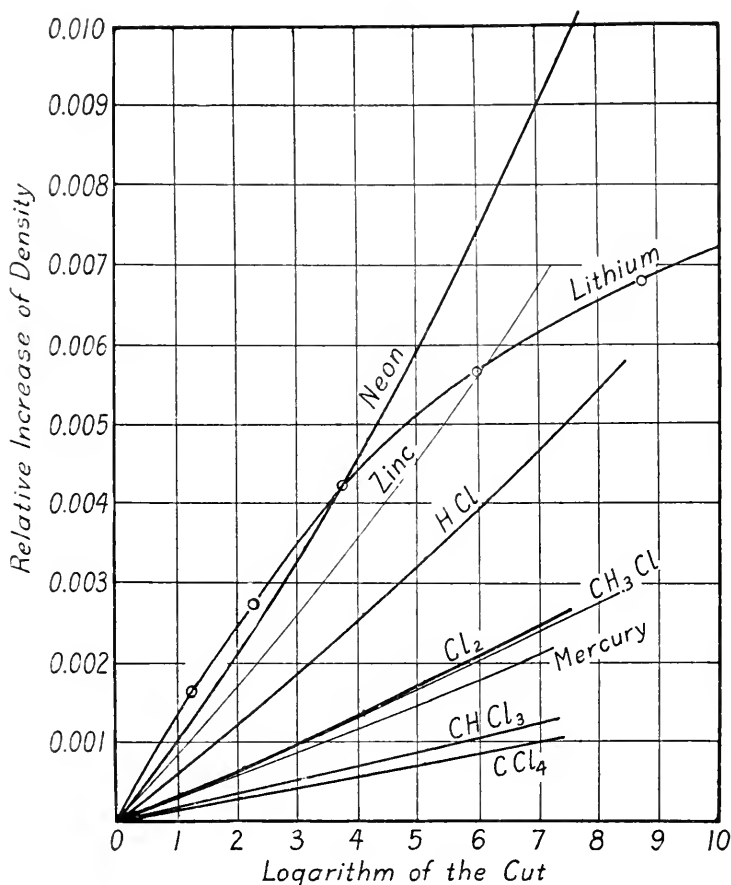
Fig. 36 shows the increase of relative density for the residue or heavy fraction of various types of isotopic mixtures. The curves for neon, hydrogen chloride, chlorine, methyl chloride, chloroform, and carbon tetrachloride were calculated for the writer by Prof. A. C. Lunn, by the use of the approximate integrated equations developed by him. The other curves were obtained from the equations of the present paper. It will be noted that most of the curves are convex toward the X-axis, which indicates that the separation becomes more rapid as it proceeds. That this is not always true is demonstrated by the curve for lithium (that for boron is similar), which shows that the separation becomes rapidly less favorable. This is due to the fact that the product of the mol-fractions increases in a mixture of two isotopes as the composition *approaches* 50 per cent. of each component, and decreases as it recedes from this value, while the rate of separation varies directly as the product of the mol-fractions. In a mixture of two isotopes, if the ordinary atomic weight is less than the mean of the atomic weights of the isotopes, as is the case with neon, chlorine, potassium, and calcium, the separation of isotopes by means of the heavy fraction becomes more and more rapid until the atomic weight of the residue increases to the mean value, and then decreases until the curve finally becomes parallel to the X-axis. *Thus the upper part of the curves for neon, hydrogen chloride, etc., have the form of the curve for lithium.* However, the cut necessary to attain the region where such substances exhibit a curve concave to the X-axis, is so great as to be practically impossible to secure.



## 78. SYSTEMATIC FRACTIONATION.

The total efficiency of a system of fractional separations of isotopes depends upon: First, the efficiency of the process used, and second, upon the fractionation plan or scheme. An ideal plan of operation is one in which there is no mixing of isotopic materials which have already been separated, but it is easy to see that

FIG. 36.



Increase in the relative density of various isotopic mixtures as the cut increases. The figure covers all of the region accessible to experiment at the present time, but it is of interest that the upper part of all of the curves is similar to that for lithium, which approaches as a limit the line 0.010. The limits approached by the other curves are much higher, but are all lines parallel to the X-axis.

this is never attained. The most nearly ideal *scheme* used thus far is that of Harkins and Madorsky for the separation of mercury as illustrated in Table XLII (Section 73), and that of Mulliken used in connection with his evaporative-diffusion. It will be seen that in one operation, as illustrated in Table XLII, the sample is divided into 8 fractions, three are lighter, and four heavier than ordinary mercury. The apparatus used for this work is such that *any number of fractions may be collected in a single*



*operation*, so the loss of efficiency by mixing may be made as small as is desired. If the fractions are made too small the number of samples of mercury may, however, become inconveniently large.

The most desirable fractionation scheme is not always the most efficient, since convenience in operation and speed are two very important factors. Thus Harkins and Broeker found it convenient in diffusing hydrogen chloride to make repeated cuts of 20 on the heavy fractions and cuts of 2 on the light fractions. Mulliken, in his application of the method of evaporative-diffusion (Section 75), in which the light fraction diffuses through the wall of a large tube of filter paper, finds that the best plan of operation for this apparatus is to allow 30 per cent. of the vapor passing up into the paper tube to diffuse through its walls. This corresponds to a cut of 1.428, the purpose of the small cut being to give a considerable decrease in the density of the diffusate, which amounts to 26.2 parts per million provided the efficiency of the process is 100 per cent. The corresponding increase in the density of the residue is 11.22 parts. Table XLIV shows the decrease in density of the instantaneous and total diffusates and the increase in density of the residue in operations of this kind. In Mulliken's process the mercury in the distillation flask becomes continuously heavier, and so would decrease in volume and weight. In order to prevent this decrease as much as possible, other heavy fractions are added to the residue. Thus if a specific experiment is begun by the use of ordinary mercury, it will be seen, for example, that when 30 per cent. of the residue has been diffused, the remaining 70 per cent. has a density 11.2 parts per million higher than that of ordinary mercury, so the volume of the mercury in the residue is increased to its initial value at this point by the addition of mercury already prepared of this same density. If the next higher density in stock happens to be 22 parts per million high, then this material is added to the residue in the flask by means of an inlet tube. The operation is stopped only after no outside heavy fractions remain to be added, and the volume of mercury in the flask becomes so low that the apparatus cannot well be operated. It can be seen that this scheme of operation is exactly that used by Harkins and Madorsky, with the exception and added advantage that the volume of the residue can be easily



increased, which is not possible with the large steel apparatus as used at present. However, a tube for the addition of mercury can easily be added to the steel apparatus, so that the general plan of operation of the two forms of apparatus can be made the same.

TABLE XLIV.

*Change of the Density of Mercury in a Diffusion Process of 100 Per Cent. Efficiency (on the Basis of the Value 0.0063 for the Separation Coefficient.)*

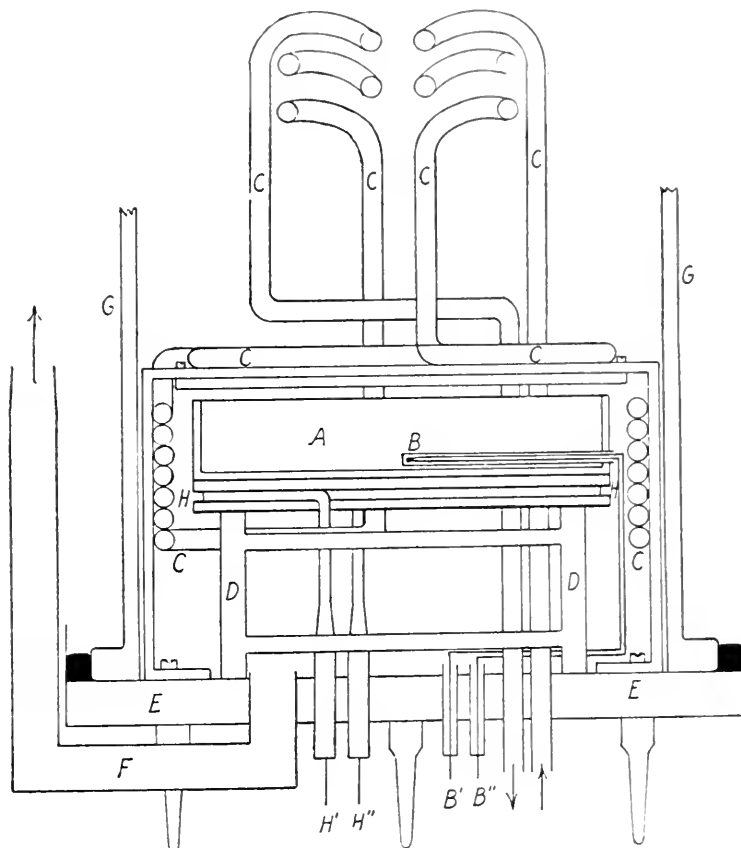
Fraction in Diffusate.	Cut.	Increase of Density in Parts per Million.		
		Residue.	Diffusate Total.	Instantaneous.
0.00		0.00	-31.4	-31.4
0.02	1.0204	0.64	-31.2	-30.8
0.04	1.0417	1.28	-30.9	-30.1
0.06	1.063	1.95	-30.6	-29.4
0.08	1.087	2.64	-30.3	-28.8
0.10	1.111	3.32	-29.9	-28.1
0.12	1.136	4.02	-29.5	-27.4
0.14	1.163	4.75	-29.2	-26.6
0.16	1.190	5.49	-28.8	-25.9
0.18	1.220	6.25	-28.5	-25.1
0.20	1.250	7.02	-28.1	-24.4
0.22	1.282	7.82	-27.7	-23.6
0.24	1.316	8.65	-27.4	-22.7
0.26	1.351	9.42	-27.0	-22.0
0.28	1.389	10.34	-26.6	-21.1
0.30	1.429	11.22	-26.2	-20.2
0.32	1.471	12.13	-25.8	-19.3
0.34	1.515	13.08	-25.4	-18.3
0.36	1.563	14.03	-25.0	-17.4
0.38	1.612	15.01	-24.5	-16.4
0.40	1.667	16.07	-24.1	-15.3
0.42	1.724	17.13	-23.6	-14.3
0.44	1.786	18.25	-23.2	-13.1
0.46	1.852	19.39	-22.8	-12.0
0.48	1.924	20.60	-22.3	-10.8
0.50	2.00	21.80	-21.80	-9.6
0.75	4.00	43.5		+12.1
0.875	8.0	65.2		33.8
0.9375	16.0	87.2		55.8
	100	145.1		114
	1,000	217.7		187
	10,000	290		259
	100,000	362		331
	1,000,000	435		404



## 79. SEPARATION OF ZINC AND CADMIUM INTO ISOTOPES.

Work on the separation of zinc into isotopes is now under way in this laboratory, and it is probable that in the preliminary experiments of Harkins and Buckner a separation of 0.04 to 0.05 unit of atomic weight has been attained, when the method of operation and the theory of the process have been taken into account. The conditions necessary for efficient operation have

FIG. 37.



Apparatus for the separation of zinc and cadmium into isotopes. *A*, trough for zinc; *B*, thermoelement; *B'*, *B''*, connections for thermoelement; *CC*, cooling coils; *DD*, glass or porcelain supporting stand; *EE*, steel base; *F*, connection to mercury condensation vacuum pump; *GG*, glass bell jar; *HH*, heating coils; *H'*, *H''*, leads to heating coils.

been so well determined by the study of mercury that the only difficulties in the process are the mechanical ones. The zinc is heated electrically in a moderately good vacuum inside a glass apparatus, and condensed on a chilled surface only about 5 mm. from the surface of the metal when the trough is full of zinc. The capacity of the apparatus (see Fig. 37) is two kilos of zinc (or anything less) for a single run. In a single run with this apparatus an atomic weight difference of 0.067 unit should be



given if on working with one kilo of zinc a 250-gram light and a 62-gram heavy fraction are obtained. Atomic weight determinations will be delayed until it is believed that the separation is 0.3 unit or more of atomic weight.

Similar experiments on the separation of cadmium into isotopes have been begun by Mr. A. A. Sunier and the writer. The isotopic composition of cadmium is unknown, but from the facts that its atomic number is even, and that it lies in the middle of the region of many isotopes, it is extremely probable that the number of isotopes is as high as five or six or more, and that the separation will be a moderately rapid one.

#### 20. CLASSIFICATION OF METHODS USED FOR SEPARATING ISOTOPES.

Mulliken and Harkins give the following outline of the principal methods which might be used for separating isotopes.<sup>110</sup>

- I. Methods using phenomena involving thermal motion of molecules and dependent on molecular velocities and their distribution. Separation necessarily incomplete.
  1. Equilibrium practically complete<sup>111</sup>—pressure and temperature constant throughout the system—inappreciable separation.<sup>112</sup>
    - A. Distillation at ordinary pressure, solution or precipitation, liquid diffusion, chemical reactions in general.
  2. Equilibrium under a pressure or temperature gradient—degree of separation proportional to logarithm of ratio of pressures or temperatures at ends of gradient, which ratio may theoretically be made indefinitely great, but practically is limited.
    - A. Equilibrium under a pressure gradient, due to gravity or rapid rotation,<sup>110</sup> or electron impact,<sup>113</sup> etc.—degree of separation proportional to the logarithm of the pressure ratio; or for centrifugal separation, to the square of the peripheral velocity, also to the product of the mol-fractions and to the square of the interval between the atomic weights of the two isotopes, but *independent of the molecular weight*.
    - B. Equilibrium under a temperature gradient (thermal diffusion<sup>114</sup>)—degree of separation approximately proportional to the logarithm of the temperature ratio; also to the product of the mol-fractions, to the square of the difference of the molecular weights of the two isotopes, and *inversely proportional to the molecular weight*.

<sup>110</sup> Compare Lindemann and Aston, *Phil. Mag.*, [6] 37, 523 (1919), who discuss in particular, methods I, 1; I, 2, A; and II, 1.

<sup>111</sup> Compare Lindemann and Aston, Ref. 27; Lindemann, *Phil. Mag.*, [6] 38, 173 (1919); Soddy, Ref. 21.

<sup>112</sup> A photochemical method of separation has been tried by Merton and Hartley [*Nature*, 105, 104 (1920)] but was unsuccessful.

<sup>113</sup> Skaupy: *Z. Physik*, 2, 213 (1920).

<sup>114</sup> Chapman: *Phil. Mag.*, [6] 38, 182 (1919).



3. Non-equilibrium processes. Flow under a gradient of partial pressure or concentration. The maximum efficiency of separation in A, B, and C, is given for zero partial pressure at the lower end of the gradient. The degree of separation in A, B, and C, is definite and limited for the light fraction, but proportional to the logarithm of the cut for the heavy fraction; while for both fractions it is proportional to the product of the mol fractions (as in thermal diffusion).
    - A. Molecular effusion and non-equilibrium evaporation.<sup>115</sup>
    - B. Molecular diffusion.
    - C. Interdiffusion of gases.
    - D. Initial effects in evaporation, diffusion, etc.
- II. Methods using phenomena in which molecules act as independent masses—separation almost complete.
1. Positive ray methods<sup>119</sup>—yields very small, though products are, theoretically, almost pure.
  2. Possibly, electrolysis of ionized liquid or gas (separation probably difficult or impossible, because mobility of isotopic ions is probably practically equal; slight differences of mobility will be masked by diffusion and convection).<sup>116</sup>

#### 81. THE TRACKS OF ALPHA PARTICLES IN GASES.

The photographs of the tracks of alpha particles secured by C. T. R. Wilson<sup>117</sup> by the use of his cloud track apparatus are of considerable interest in connection with the study of the structure of the atom. Some of the tracks indicate that an alpha particle is occasionally turned very sharply from its initial path, presumably by approaching very closely to the nucleus of an atom, as is evidenced by the sharp spurs which result. Shimizu<sup>118</sup> has devised a modification of this apparatus which gives two expansions per second of the chamber which contains the water vapor. Thus two complete sets of alpha ray tracks can be observed visually, or photographed, every second, so that 7200 photographs can be secured in a single hour of operation.

<sup>115</sup> The method of irreversible condensation of a vapor or gas in a special case of the method of molecular effusion, and is thus somewhat similar to irreversible evaporation. J. J. Thomson's suggestion [*Proc. Roy. Soc.*, 99A, 87 (1921)] that the isotopes of chlorine might be separated by fractional absorption of hydrogen chloride in an alkaline solution would make use of this method. This would hardly be practical, however, due to the rapidity of the absorption and the consequent impossibility of good mixing. If air were admixed with the hydrogen chloride, there might be some degree of separation as a result of gaseous diffusion.

<sup>116</sup> See also Lindemann, *Proc. Roy. Soc.*, 99A, 87 (1921).

<sup>117</sup> C. T. R. Wilson: *Proc. Roy. Soc.*, A87, 1277-92 (1922).

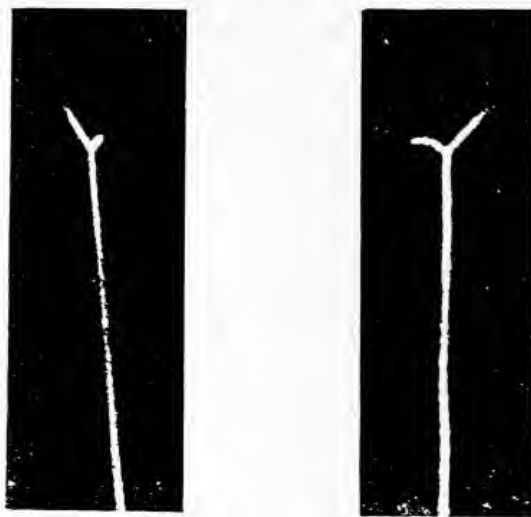
<sup>118</sup> Shimizu: *Ibid.*, 99, 425-35 (1921).



With this apparatus Shimizu made the interesting observation that about one in three hundred of the alpha ray tracks is *branched* at the end, as in Fig. 38.

Mr. R. W. Ryan and the writer have constructed two models of the Shimizu apparatus, one with an expansion chamber 8 cm. in diameter, and a much larger apparatus in which the diameter is 13.3 cm. The smaller apparatus is shown in Fig. 39. With this many branched tracks have been found, but their relative number does not seem to be so great as that found by Shimizu. Fig. 40*a* shows 9 or 10 quite straight tracks from a single source,

FIG. 38.



Photograph of a branched  $\alpha$ -ray track viewed from two positions at right angles to each other as taken by Shimizu. Actual magnification 5.5.

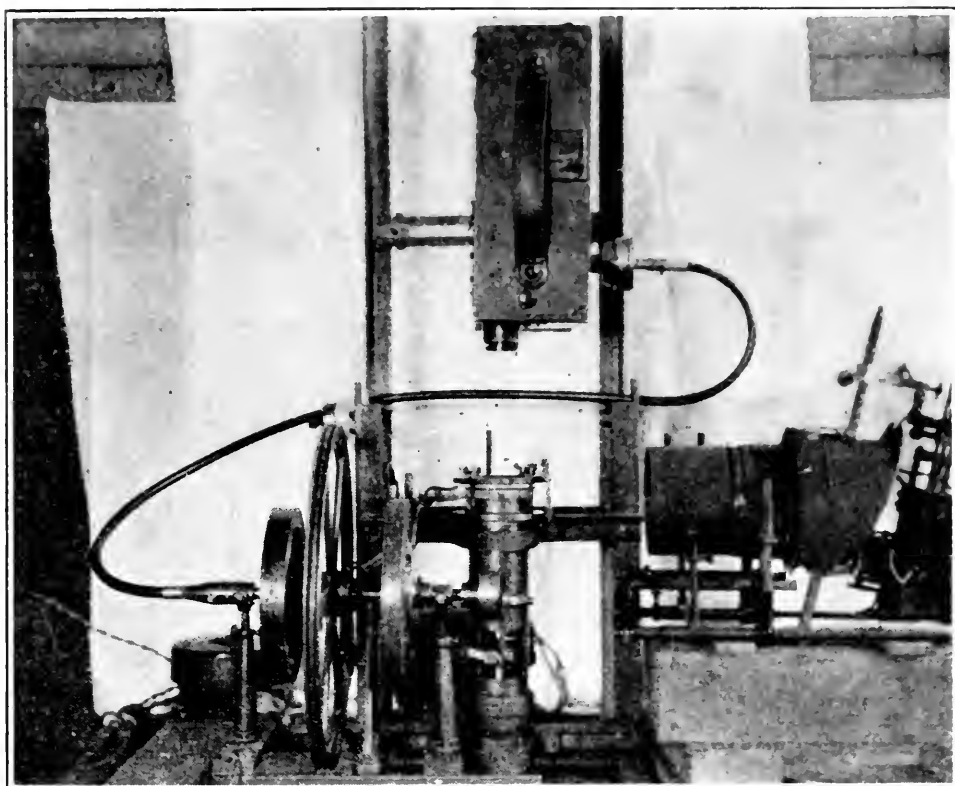
with one track at right angles that represents an alpha particle which was later in crossing the field of view than two of the other alpha particles. It will be seen that when this occurs the tracks of the particles which shoot through earliest reduce the supersaturation of the water vapor to such an extent that the particles which pass later leave no visible tracks in their immediate vicinity.

Fig. 40*b* represents one alpha particle which was turned through a sharp angle very close to the source, and another which gives a branched track at the end, though the branching may not show clearly in the reproduction. Fig. 39*c* is of considerable interest since it gives a branched track, one of the branches of which is about 2 centimetres long. Unfortunately this photograph was taken in only one plane, so it is impossible to determine the length of the other branch. That some alpha particles are turned



through as much as a right angle may be seen in Fig. 40*d*, while 40*e* shows a branching which occurs near the source of the particle. Figs. 40*f* to 40*i* are typical sets of tracks taken from the series of several thousand photographs thus far secured. A number of lenses have been tried, and the best results secured by

FIG. 39.



Apparatus for photographing the tracks of alpha particles. (Shimizu-Wilson apparatus as modified by Ryan.)

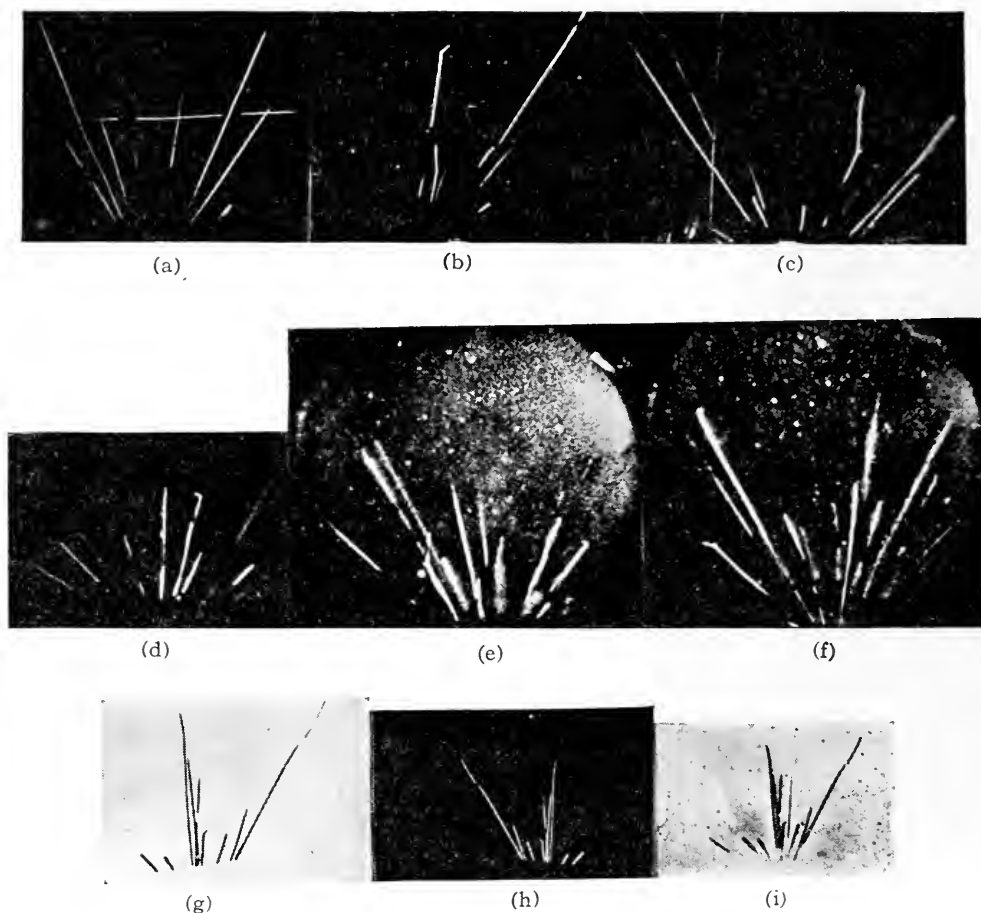
the use of a Cooke F2 cinematograph lens in connection with a Universal Moving Picture Camera.

The interest in the branched tracks lies in the idea that while one branch may be due to the alpha particle projected by the radioactive source (polonium in these specific experiments, though radium-C will be used later), the other branch is probably due either to the atom nucleus which is hit, or to an alpha particle which is disrupted from the nucleus. It is hardly probable that it can be due to a disrupted H-particle (proton) since the path of such a light particle should be much longer. If it can be proved that an alpha particle is disrupted from the nucleus in any of these



branchings of the path, the result would be of extreme importance since thus far there is not the slightest evidence that anything other than hydrogen has been produced in the *artificial* disruption of atoms, though it is well known that helium is produced in the *natural* disintegration of the radioactive elements. Both Shimizu

FIG. 40.



Alpha ray tracks in air. The actual full length tracks are about six cm. long, so the reproductions are from one-third to one-half natural size. These photographs have not been retouched.

and Rutherford have in mind the idea that these branched tracks may be an indication that the nucleus of the atom is disrupted.<sup>119</sup>

A single run of 4000 photographs, as made in this laboratory, gave about 25 tracks which spread into two branches at the end. In one of these a remarkable branching occurred (Fig. 41), since

<sup>119</sup> The work of Mr. Ryan and the writer has been greatly delayed by the lack of a good lens for this work, but the lens now in use is well adapted for this purpose.



one of the tracks is shot almost directly backward (actually turned through an angle of  $130^\circ$  instead of  $180^\circ$ ) while the other is at an angle of about  $20^\circ$ . In the projection on the photograph the angle of incidence and of reflection are almost equal. Such tracks are of great importance in the study of the problem, but a large number of them must be secured before definite conclusions as to their meaning are warranted. It seems probable,

FIG. 41.



Alpha ray track with forward and backward branches (Ryan and Harkins).

FIG. 42.



Alpha ray track with right angle turn.

however, that the forward track is due to an oxygen or nitrogen nucleus and the backward track to the deflected alpha particle. The kinetic energy of the alpha particles given off by some of the radioactive substances is so extremely great that it seems difficult to conceive that even nuclei built of alpha particles alone will resist disruption in all cases. However, the number of disruptions may possibly be so small that no statistical evidence of their occurrence can be obtained by the use of the present form of apparatus, which, while it possesses the great advantage that it makes almost the whole of the track of the alpha particle visible,



has also the great disadvantage in comparison with Rutherford's scintillation method, that the cloud track method cannot be used when the number of alpha particles is large. In the scintillation method, on the other hand, millions of alpha particles per second may be used, since the screen used is placed beyond the range of all of the alpha particles used as projectiles.

Mr. Ryan and the writer have observed a number of longer range tracks which occur when the alpha particles pass through paraffin. These seem to have a different appearance from the ordinary alpha ray tracks. On account of the lack of a sufficiently powerful radioactive source, it has been impossible to determine whether these are caused by H-particles or not. If they should prove to be such particles it would be possible to demonstrate photographically the disintegration of elements of the type of aluminium and nitrogen. The H-particles produce a smaller ionization than alpha particles.

Interesting experiments by Kenoshita, Ikeuti, and Akiyama,<sup>120</sup> made with the original Wilson apparatus, give photographs in which two alpha ray tracks originate at a common point in the gas of the apparatus. Each point represents the position of an atom of actinium emanation which at the moment disintegrates into AcA, and 0.002 second later into AcB.

## 82. THE BUILDING AND EVOLUTION OF ATOMS.

Early in 1915 Harkins and Wilson published the first definite theory that the nuclei of light atoms are built up from alpha particles and hydrogen nuclei (positive electrons). The present paper reviews their theory and presents the experimental evidence collected by the writer in its favor. This evidence is so comprehensive that it cannot well be summarized in this section, but it may be noted that the figures and tables of the present paper<sup>121</sup> give the most conclusive evidence, presented *prior* to the disintegration of certain light elements into hydrogen, that the principal group involved in the building of the light atoms is the alpha particle. It is the opinion of the writer that not only is this true, but that at the present time *the experimental chemical data*

<sup>120</sup> Tracks of  $\alpha$ -particles emitted by actinium emanation and actinium A. S. Kenoshita, H. Ikeuti and M. Akiyama, *Proc. Phys. Math. Soc. Japan*, **3**, 121-33 (1921) *Sci. Abs.*, **25A**, 52, (1922).

<sup>121</sup> Particularly in Figs. 12, 13, 14, 19 and 21, and in Tables XXVI, XXVII, III, IV, XII, XXII, XXIII, and XXIV.



*summarized here give much more conclusive evidence for the building of the light atoms from alpha particles than the disintegration experiments themselves.* That this is the case will be realized by anyone who makes the considerable effort necessary to thoroughly digest the great mass of evidence presented. The fact that the light elements give exactly the same form of "map" (Fig. 19) as the radioactive elements; the fact that Fig. 12 exhibits periodicities of 2 and of 4 in both directions, these being the value of the charge and mass of the alpha particle; and the importance of the numbers 2 and 4 in the abundance relations of the elements and atomic species, give the strongest, though possibly not the most simple, evidence for this point of view.

The theory is essentially one of the building and evolution of the atomic species.<sup>122</sup> It differs from the theory of Nicholson which preceded it in that it can find no place thus far for the hypothetical elements coronium, nebulium, protofluorine, etc., but makes use of a known element, hydrogen, as its fundamental building stone, and of a second known element, helium, as the

---

<sup>122</sup> Aston (page 116, "Isotopes") classifies the writer's theory as a "disintegration" as opposed to the more "attractive (evolution) theory," thus showing that he has not read even the titles of the first papers of the series. Thus he has missed the statement in the second paper (1915) "the evidence presented in these papers, which seems to show that the elements are atomic compounds of hydrogen and helium, appears to give some support to the theory of the evolution of the heavier atoms from those which are lighter." The third paper of the series (published in 1916 and again in 1917) is entitled "The Evolution of the Elements and the Stability of Complex Atoms," and another paper published at the same time was entitled "The Building of Atoms." It is my own opinion that Aston underestimates the effects of the atomic disintegrations, but his classification of the writer's viewpoint as a disintegration, as opposed an evolutionary theory, is altogether incorrect as the above titles show. His statements as to the success of predictions of the existence of isotopes, as given on page 117, are equally incorrect and misleading. It is unfortunate that Aston believes that the ideas of evolution and of disintegration are altogether opposed and exclusive of each other, since the more rational viewpoint is that both are of prime importance. The writer has felt that the nuclei of light atoms have been mostly built up from alpha particles and hydrogen nuclei, but it is not a necessary conclusion that all light atoms are permanently stable just because they are built from a relatively small number of particles. In fact, Fig. 21 and other similar figures of the present paper indicate that the stability of the light atoms decreases very much more rapidly than that of the heavy atoms when they depart from the region of stability by a certain number of neutrons ( $pe$ ).



most important secondary unit. It agrees in general with the astronomical theory of the evolution of the elements from lighter to heavier, in the stars, though it is much more specific and is based upon much more extensive evidence than the astronomical theory. The bearing of the astronomical evidence is much more in doubt, since the changes in the spectra of the nebulae and the stars, in which hydrogen and helium are supposed to appear first, and then to change gradually into calcium, magnesium, oxygen, iron, etc., might possibly be due to the conditions of excitation of the spectra and the segregation of the elements in these bodies. Also the evolution of the stars may not be in the supposed order. The writer is not opposed to, but rather is in favor of, the astronomical theory of evolution, but it is nevertheless of importance to point out that the evidence which it presents in this connection is as yet faulty.

The importance of the writer's whole number rule for the atomic weights of the elements other than hydrogen is now well recognized. When taken in connection with the theory of relativity it indicates, as was first pointed out in 1915 by Harkins and Wilson, that the *only* source of enormous amounts of heat (other than that of radioactive changes) such as would account for the excessive amount of heat given off by the sun and by the giant stars, is to be found in the union of hydrogen to form helium, which, for one pound of hydrogen, gives an amount of energy corresponding to that liberated in the combustion of 10,000 tons of coal.<sup>123</sup>

---

**Department Store Laboratory.**—E. B. MILLARD (*Jour. Ind. Eng. Chem.*, 1922, xiv, 785–786) gives a resumé of the work done in the chemical laboratory of a department store. The routine work consists chiefly of determinations of the wool or silk in materials, and especially the detection of artificial silks, also tests of the fastness of dyed fabrics to perspiration, sunlight, washing, or water spots. The coal used in the power plant, and the milk used in the restaurant are analyzed at frequent intervals. The laboratory also makes examinations in connection with the adjustment of claims of unsatisfactory materials. New materials are analyzed as they appear on the market. The information obtained is placed at the disposal of both the purchase and the sales divisions of the organization. J. S. H.

---

<sup>123</sup> For the calculation of the amount of energy liberated see section 22 of the present paper.



## NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

### THEORY, CONSTRUCTION, AND USE OF THE PHOTOMETRIC INTEGRATING SPHERE.<sup>1</sup>

By E. B. Rosa and A. H. Taylor.

[ABSTRACT.]

DURING the last fifteen years great progress has been made in the production and utilization of light. With this progress has come the necessity for greater precision in the measurement of light output, and the Ulbricht photometric integrating sphere has been extensively utilized for this purpose. It is the only available instrument by which the total light output of sources can be determined in one measurement. There is no complete treatment of the theory, construction, and use of the sphere available in English. This paper has been written to meet that need, and should be of interest to all who are concerned with photometry.

The majority of the spheres in use to-day are built of shaped sheet metal segments fastened to structural steel. Such spheres can be made of fairly light but substantial construction, but they are expensive to build. In the smaller sizes a cheaper construction may be realized by the use of papier-maché globes such as are used in schools.

In 1915 the authors designed and constructed an 88-inch reinforced concrete sphere at the Bureau of Standards. Steel T-rails were shaped into circular arcs and fastened to metal rings at each end, thus forming ribs of a spherical framework. These ribs were fastened together with metal bars and expanded metal lath, and the whole was plastered with concrete in the proportion of one part Portland cement to two and one-half parts sand. The interior was swept out to a true spherical shape by means of a special sweep hinged at the centre of a pipe placed on the vertical diameter of the sphere. Later both interior and exterior surfaces were finished with white cement, giving a wall about one to one and one-half inches thick. A concrete sphere such as this, especially in the larger sizes, can probably be constructed more economically than a metal sphere of the same size.

---

\* Communicated by the Director.

<sup>1</sup> *Scientific Papers*, No. 447.



This sphere has been thoroughly tested and found to give accurate results for many types of light sources. The sources tested included vacuum lamps both bare and with several types of glass reflectors and globes and a metal reflector. In all cases the agreement of the results with those obtained by point-by-point integration was practically within the range of ordinary errors of photometric measurements. Considerable care is necessary in the use of the sphere for measuring light sources which differ appreciably in their absorption of light, and in order to obtain reliable results on such sources proper corrections must be determined and applied.

The requirements for a satisfactory paint for photometric spheres are rather severe, and since no commercial paints fulfilling these requirements could be found, it was necessary to develop one. A good paint for this purpose is composed of alcohol, camphor, celluloid, and zinc oxide. It has a very high reflection factor, and does not discolor with age. The photometric equipment consists of a bar photometer, Lummer-Brodhun contrast photometer head, sectorized disks, recording drum, and magnet, etc. The "substitution" method of photometry is used.

The theory of the sphere has been investigated, and tests have been made to verify certain phases of it, with satisfactory results. The best size and position of the opaque screen have been theoretically determined. It is found that as the lamp approaches the sphere wall at a point screen from the observation window, the brightness of the latter is reduced. This is due to the fact that as the lamp approaches the wall more of the direct light flux falls on the zone screened from the observation window, and hence it must be reflected from the sphere wall at least twice before it can reach the window.

One source of error in the use of such spheres is often overlooked. If the lamp being tested is somewhat blackened, or has parts which absorbed a considerable portion of light, the amount of light which it absorbs in the sphere will increase as it approaches the sphere wall. The amount of light absorbed by the lamp is also greater when the reflection factor of the sphere walls is high. These facts are of great importance if life-test lamps, appreciably blackened, are being photometered. It can be shown theoretically that a sphere to be used for life-test measurements of incandescent lamps should be painted with a paint having a reflection factor



of about 80 to 85 per cent. in order to minimize the errors of measurement.

The theory of the sphere assumes that its surface is a perfect diffuser, that is, that the specific brightness of any area is independent of the angle of view. Measurements of the diffusion characteristics of the sphere paint and the milk-glass observation window have been made. These show that the error arising from the measurement of a narrow beam of light in terms of a perfectly diffused light, or of light uniformly distributed in the sphere, is practically zero when the beam is directed at the sphere wall at a point about  $80^\circ$  on the circumference from the window.

The original paper also contains a bibliography of the subject.

---

#### PROPERTIES OF ELECTRICAL INSULATING MATERIALS OF THE LAMINATED, PHENOL-METHYLENE TYPE.<sup>2</sup>

By J. H. Dellinger and J. L. Preston.

[ABSTRACT.]

THE manufacture of phenolic synthetic resins as applied to the fabrication of electrical insulating material has only become commercially important within the last twenty years. Three men might be mentioned who have been instrumental in the development of these resins and the resulting insulating material in this country, namely, Messrs. Jonas W. Aylesworth, Leo H. Baekeland, and L. V. Redman.

This type of insulating material was developed to meet a real commercial need. Experience had shown that insulating materials using shellac, bituminous and similar materials as a binder, and hard rubber, hard fibre, glass, porcelain, amber, celluloid, and other materials had certain mechanical or electrical defects. The phenolic insulating materials were developed to correct some of the major weaknesses inherent in the other types, but to the conservative investigator the phenolic materials are not believed to be a panacea for all insulation troubles. These phenolic materials, as an example, are not substitutes for hard rubber though they are advantageously used to replace hard rubber in many places. Hard rubber softens, warps, and discolors when left in the sunlight or exposed to moderate heat. The phenolic materials apparently do not. The price of the better grades of hard rubber is already quite high and is increasing, while the price of phenolic insulating

---

<sup>2</sup> *Technologic Papers*, No. 216.



materials should decrease as the knowledge of the art increases. Properly made and properly protected hard rubber is superior electrically to the phenolic materials. The average value of phase difference, that is, the dielectric power loss, for the phenolic insulating materials, is four to eight times that for hard rubber. The phenolic synthetic resins have a wide variety of uses in many fields, including the manufacture of decorative beads, cigarette holders, noiseless gears, sword scabbards, and conductor tubes in vinegar factories. It is, however, in the manufacture of electrical insulating materials that they find one of their most important applications.

The materials manufactured using the phenolic synthetic resins may be broadly classified as laminated materials, or moulded materials. As indicated by the title, this paper is concerned exclusively with materials of the laminated type. Unlike the laminated materials, the moulded materials can be formed into intricate shapes without machining. They therefore have a wide variety of applications. It is expected that a publication supplementing this paper will be published later, giving some data on moulded materials.

The materials referred to in this paper as of the laminated, phenol-methylene type are those made by building up sheets of paper, fibre, or fabric, which had been previously impregnated or coated with phenolic (synthetic) varnish to some desired thickness and then subjecting the stack to comparatively great pressure in a heated hydraulic press. The varnishes used in the manufacture of these materials were Bakelite, Condensite, and Redmanol, manufactured respectively by the General Bakelite Company, Condensite Company of America, and The Redmanol Chemical Products Company. These varnishes are all somewhat similar in that they depend on chemical reaction and are all synthetic. The chemical reaction of the varnish is retarded so that it can be shipped to the consumer or stored for some time (the length of time depending on the type of varnish). When the varnish is subjected to heat, the reaction is again started and tends toward completion at a rate depending on the temperature. This heating is done after the filler (paper, etc.) has been impregnated or coated with the varnish and the stack placed in the press. The pressure (with heat) has a tendency to produce from the separate sheets, a dense homogeneous sheet of insulating material.



This paper is meant to serve as a compilation in a form convenient for reference on the electrical, mechanical, chemical and thermal properties of the laminated sheet insulating material of the phenol-methylene type manufactured in the United States; on the methods of testing the electrical, mechanical, chemical and thermal properties; and on books, periodicals, and patents dealing with tests on or properties of insulating material.

Radio-frequency phase difference or power loss, dielectric constant, and flashover voltage, direct current surface resistivity and volume resistivity, tensile strength, modulus of elasticity (tensile), proportional limit, modulus of rupture, modulus of elasticity (transverse), Brinell hardness, scleroscope hardness, impact strength, permanent distortion, density, moisture absorption, machining qualities, thermal expansivity, and the effects of heat, acid, and alkali have been considered in this paper, and data or statements are given relative to these properties. Other data are also given which have not been determined at this Bureau. These data include values on dielectric strength or puncture voltage, crushing strength parallel with and perpendicular to the laminations as well as moisture and oil absorption when the time of immersion was longer than in the Bureau of Standards tests.

Much space in this paper is devoted to the description of the methods of testing. This seems quite necessary because some of the numerical data are in part a function of time, voltage, pressure, etc., as well as of the mechanical arrangement of the testing apparatus. Such a description of testing methods serves other purposes. Many of the methods were developed at the Bureau of Standards after much experimental work. The methods are described in detail so that they may be available to others who wish to do such testing, and with the hope that constructive criticism may be stimulated which will result in improved methods.

A part or all of the above-named tests have been made on fifteen grades of laminated, phenolic insulating material as manufactured by the four manufacturers in the United States. The manufacturers of the several grades are given in the following alphabetical order:

Diamond State Fibre Company.—Condensite Celoron: grade 10, fibre base; grade 15, fibre base; grade 20, fabric base.

The Continental Fibre Company.—Bakelite-Dilecto: grade XX, paper base; grade X, paper base; grade C.B., fabric base.



The Formica Insulation Company.—Formica: grade M, paper base; grade M-2, paper base; grade P, paper base; grade R, fabric base.

Westinghouse Electric and Manufacturing Company.—Bakelite Micarta: grade 32-X, paper base; grade 21-X, paper base; grade 323, paper base; grade 213, paper base; grade 21-D, fabric base.

These grades cover all that were in general use at the time this research was started. Other grades have appeared since, but as a rule they are not fundamentally different from some one of the grades reported in this paper.

The data are arranged in such a manner that it will be directly usable by persons having different problems involving this type of insulating material.

First, there is a detailed record of data for all thicknesses of all makes and grades of material considered in this paper. This should assist the engineer in determining the effects of various electrical or mechanical stresses applied to the material or the effects of changes in the material on the electrical or mechanical properties. As an example this paper should assist him in determining the probable effect on phase difference or power loss of the season of the year, baking or drying, frequency variation, thickness, color or dye, and surface finish. He could also get an idea of the effect of the grain of the insulating material on tensile and transverse strength properties. Many other examples might be given of the use of the detailed data.

Second, the data have been summarized. In this summary the data on the various materials, grades, and thicknesses have been kept separate. It is somewhat similar to the detailed record except that the results of many measurements on any one sample have been averaged and recorded.

Third, here the detailed data have been averaged and recorded regardless of thickness. This gives the engineer a general idea of the individual characteristics of the various makes and grades. It is a very condensed summary.

Fourth, a summary-comparison table has been prepared and included in this paper. Average values for the various properties of laminated phenolic insulating materials are given regardless of make, grade, or thickness. In this same table the properties of hard rubber, hard fibre, laminated phenolic, and moulded phe-



nolic materials have been recorded in a manner to show how they compare. For one desiring only very general information, this table should be quite useful.

---

## RESULTS OF SOME COMPRESSION TESTS OF STRUCTURAL STEEL ANGLES.<sup>3</sup>

By A. H. Stang and L. H. Strickenberg.

[ABSTRACT.]

THIS article presents the results of compression tests of 170 structural angles, made at the Pittsburgh branch, Bureau of Standards. The object of the tests was to determine the ultimate compressive strength of angles fastened at the ends in such ways as would closely correspond to their connections in the construction of transmission towers. There was also tested a series of angles with square ends. An end fixation factor was found to represent satisfactorily the effect of different types of end connections.

The values of the maximum unit load in these tests vary over a considerable range for any given slenderness ratio and manner of fastening the angles in the testing machine.

In most cases the specimen which sustained the greatest unit load for a given slenderness ratio and method of fastening suffered the least lateral deflection and the angle which bent most sustained the lowest unit load at failure, the deflection being measured at  $4/9$  of the theoretical maximum load.

For large slenderness ratios the average values are well represented by Euler's formula for long columns, calculated for different values of the end fixation factor.

The Kármán curves, recalculated for a yield point of 37,000 lbs./in.<sup>2</sup> and modulus of elasticity of 30,000,000 lbs./in.<sup>2</sup> represent the average results for small slenderness ratios for several methods of end fixation, except in the neighborhood of  $l/r = 80$  to 85, where the effect of eccentricity was greatest. The values of the end fixation factor are given.

For angles with ends folded the column formulas considered do not represent the results found in this series of tests.

It is believed that the values of end fixation factor are of importance in the design of structures where the end conditions

---

<sup>3</sup> *Technologic Papers*, No. 218.



approximate those used in these tests, no matter what formula the designer prefers to use.

Eccentricity of loading produces a diminution of column strength. In these tests the greatest effect of eccentricity was observed in the neighborhood of a "free length" corresponding to  $l/r=85$ , which agrees with the results of Kármán's investigations.

---

#### TEST OF A HOLLOW TILE AND CONCRETE FLOOR SLAB REINFORCED IN TWO DIRECTIONS.<sup>4</sup>

By W. A. Slater, Arthur Hagener, and G. P. Anthes.

[ABSTRACT.]

A LARGE slab, 48 by 115.5 ft. centre to centre of outer supporting girders, was loaded. In the 48-ft. dimension the slab was divided into three spans of 16 ft. each. In the 115.5-ft. dimension it was divided into six spans, two end spans were 16 ft. each, the two middle spans 19.25 ft. each, and the two spans at the other end were 22.5 ft. each. The slab was therefore divided into 18 panels, of which six panels were 16 ft. square, six panels were 16 by 19.25 ft., and six panels were 16 by 22.5 ft. Girders extended along all panel edges, and columns stood at all intersections of girders. The slab was 6 in. thick over all and was made up of 6 by 12 by 12 in. clay tiles laid in rows parallel to the panel edges with ribs of concrete 4 in. wide and 6 in. deep between rows of tiles in both directions. Each concrete rib was reinforced with one  $\frac{1}{2}$ -in. round bar in the top for negative moment and with the same in the bottom for positive moment. The bars for negative moment extended out into the panel one-fourth of the span length in the direction of the bar and were there hooked for anchorage.

The slab reinforcement had a yield point of about 54,000 and the girder reinforcement of about 46,000 lb. per sq. in.

According to current methods of design the working loads (sum of live and dead loads) for the three sizes of panel would be 83, 67 and 48 lb. per sq. ft. for the square, intermediate-size, and long interior panels, respectively. The weight of the slab was approximately 50 lb. per sq. ft.

For about two months the square panels stood under a uni-

---

<sup>4</sup> *Technologic Papers*, No. 220.



form load (sum of live and dead loads) of about 450 lb. per sq. ft., the intermediate-size panels under 330 lb. per sq. ft., and the long panels under 280 lb. per sq. ft. The load was then shifted and (with smaller loads on adjoining panels) the loads for the succeeding six months on certain panels were: square panels, 780; intermediate-size panels, 655, and long panels, 555 lb. per sq. ft. Finally the load was concentrated still more and for about eleven months the loads on single panels of each size have been: square panels, 1463; intermediate-size panels, 1234, and long panels, 970 lb. per sq. ft.

During the loading strain gage readings of elongation and shortening were taken at about 1600 critical places in the concrete and in the reinforcement. The negative moments for the 16-ft. spans of the interior panels based upon these stresses (observed after maximum uniform loads of 450, 330, and 280 lb. per sq. ft. had been in place about two months) with an allowance for dead load stresses, were  $0.0186 Wl$  for the square panels,  $0.0277 Wl$  for the intermediate-size panels, and  $0.0398 wl$  for the long panels. The negative moment in the direction of the long span was  $0.0213 Wl$  for the intermediate-size panels and  $0.0179 Wl$  for the long panels, where  $l$  is the short span.

The coefficients for the exterior panels averaged about 20 per cent. greater than the coefficients for the interior panels.

Both the deformations and the deflections increased when the load remained constant over a considerable time, but the fact that so great a load has been carried for so long a time without excessive deflection removes any misgiving as to the adequacy of the form of construction used.

The deflections at the centres of the interior panels observed after the maximum uniform load had been in place about two months averaged  $1/273$ ,  $1/563$ , and  $1/1800$  of the clear short span for the squares, intermediate, and long panels respectively. Upon removal of 80 per cent. of the load the recovery was 50 per cent. of the original deflection or more.

At this stage of the test the largest crack was less than 0.01 in. wide. The largest crack in the under side of the slab under a load of about ten times the design loads stated in a previous paragraph was about  $1/40$  in. wide.

The points of zero stress in the negative reinforcement occurred at about one-fifth points of the spans.



Under the greatest loads applied the shearing stresses in the ribs of the slab were 405 lb. per sq. in. or more assuming the tile walls to have been effective in resisting shear. If the resistance of the tile walls is neglected the shearing stress must have been 500 lb. per sq. in. or more.

The estimated shearing stress in one of the girders is 440 lb. per sq. in. The loads on which these shearing stresses are based had been on the slab for nearly a year.

---

### THE MAGNETIC SUSCEPTIBILITY AND IRON CONTENT OF CAST RED BRASS.<sup>5</sup>

By L. H. Marshall and R. L. Sanford.

[ABSTRACT.]

THE presence of iron in commercial brass is often objectionable, particularly if it occurs as discrete, poorly alloyed particles. In order to obviate any such harmful effects, a very low ferrous content is frequently specified. Therefore, a rapid, non-destructive method for quantitatively determining its presence would be of great value in practice. A magnetic method of inspection would fulfill the requirements of such a test if a definite relationship exists between some magnetic property and the iron content of the metal. From the meagre information available in the literature it was evident that this matter had received little attention.

With these facts in mind a study was made of the magnetic properties of cast tin red brass contaminated with iron. A series of seven samples of an alloy of the type 82 copper, 15 zinc, 3 tin was prepared containing various small proportions of iron up to 0.75 per cent. These specimens were magnetized in a suitable solenoid. A test coil of 1200 turns extended over two-thirds of the specimen and readings of the magnetic induction were taken by means of a ballistic galvanometer. Greater precision was secured by balancing out the magnetizing force by means of a variable mutual inductance, so that the galvanometer deflection, in each case, was a measure of the increase in flux density due to the specimen (metallic induction).

Magnetic properties were determined in the cast condition and after annealing 15 minutes at 625° C., 8 hours at 800° C.,

---

<sup>5</sup> *Technologic Papers*, No. 221.



and 16 hours at 800° C. for different values of magnetizing force up to 500 gilberts per cm. The microstructure of the metal was determined before and after these various heat treatments. The cored structure of the cast material largely disappeared after the first eight-hour anneal. The eutectoid present in the cast samples was likewise absorbed at this time. The second eight-hour anneal caused no further change in structure. Oxide inclusions were present in all of the samples. Up to 0.14 per cent. the iron went into solid solution in the matrix of the alloy, but larger amounts than this caused the appearance of pale, rounded areas of an iron rich constituent. A rough estimate of the iron content could be made from the number and size of these areas. The percentage of iron present had no noticeable effect on the grain size of the metal, nor did the grain size have any definite influence on the magnetic properties of the specimens.

The data obtained revealed several interesting points. For instance, the magnetic properties are not a precise index of the iron content of the cast metal. Then the magnetic susceptibility is markedly affected by changes in physical condition produced by heat treatment. Even after the material has been thoroughly annealed, there is still no simple relationship between the magnetic susceptibility and the iron content. The seeming irregularities in the magnetic behavior of these brass samples were probably due, in the case of the cast specimens, to the unhomogeneous structure of the metal; while those of the annealed bars were caused by the presence of the iron as two modifications, the dissolved and the segregated. The iron content was the source of the magnetic effects observed.

---

**RELATIVE USEFULNESS OF GASES OF DIFFERENT HEATING  
VALUE AND ADJUSTMENTS OF BURNERS FOR CHANGES  
IN HEATING VALUE AND SPECIFIC GRAVITY.<sup>6</sup>**

By W. M. Berry, I. V. Brumbaugh, J. H. Eiseman, G. F. Moulton,  
and G. B. Shawn.

[ABSTRACT.]

IN connection with an investigation conducted by the Public Service Commission of Maryland to determine the most economic heating value standard for manufactured gas in the city of Balti-

---

<sup>6</sup> *Technologic Papers*, No. 222.



more, the Bureau of Standards conducted an extensive series of laboratory tests to determine primarily: (1) The relative utilization efficiency of gases of different heating value; (2) the extent to which present appliances can be adapted to give good and efficient service with gases of different heating value and composition; and (3) what adjustment in appliances is necessary to give the consumers good and efficient service when different kinds of gases are mixed and there is a variation in the composition, heating value, and the specific gravity of the gas.

After giving due consideration to a number of factors that have an influence on efficiency, it can be stated that the results of the laboratory tests of gases varying in heating value from 300 to 600 Btu per cubic foot indicated that the usefulness for top burner cooking is dependent almost entirely upon the total heating value per cubic foot. Thus, to heat a given quantity of water to the same temperature in the same time required two cubic feet of 300 Btu gas to one cubic foot of 600 Btu gas. In other words, the quantity of gas required varied inversely with the heating value of the gas.

*Over the range of usual operating conditions the efficiency of heat absorption varies only slightly with a change in the rate of heat supply.* With the star type of burner and an average size vessel, the efficiency varied from about 36 per cent. at 7000 Btu per hour to 37.7 per cent. at 11,000 Btu per hour.

Burners can be operated over a somewhat greater range of adjustment with coal gas than with water gas. The tests show that with coal gas the yellow flame occurs at a higher Btu per cubic foot of mixture (lower air-gas ratio). On the other hand, with coal gas it is practicable to operate burners with a lower Btu per cubic foot of mixture (higher air-gas ratio) without having the burners flash back.

The results on the whole show that present domestic range burners can be adjusted to give satisfactory service over a wide range in heating value, the slight differences in behavior of the different gases not being of sufficient importance to have much weight in any consideration of their relative merits for use in domestic appliances. Some change in size of orifice and air shutter adjustment of burners is necessary to secure the best service when a material change is made in heating value, but



most existing burners can be readily adjusted to give good service with heating values as low as 450 Btu without alterations of the burners.

The practice of mixing different gases has become quite common as a result of the development in coke-oven processes with the production of by-product gas, the building of combination coal and water gas plants, and the necessity of supplementing natural gas with different kinds of manufactured gas. Uniformity in heating value, specific gravity and pressure are essential for the very best service, yet it is practicable to adjust burners to give satisfactory service in cities where different gases are mixed and there is considerable variation in the heating value or specific gravity.

---

**Investigations of Crystalline Structure by Means of X-rays.** F. KIRCHNER. (*Ann. d. Physik*, No. 17, 1922.)—When a substance is obtainable in large, perfectly formed crystals it is possible from the application of X-rays to determine with great exactitude the dimensions of the crystal structure. When, on the other hand, the substance is not so existent the Debye-Scherrer method for powdered crystals may be applied but the accuracy of the results is much less. There is another method, that of Seeman and Bohlin, in which the rays are brought to a focus after reflection from the metal under investigation. Kirchner shows how to improve the technic of this method and how to derive more accurate dimensions by its use. He succeeded in getting data on the structure of copper from .002 milligram of the metal deposited on a sheet of aluminium.

An alloy of iron and nickel containing 25 per cent. of the latter was long ago shown by Hopkinson to possess remarkable magnetic properties. It can be magnetized provided it has been strongly cooled, its permeability then being roughly equal to that of hard nickel. If the alloy be heated to  $580^{\circ}$  it ceases to be magnetic and remains in this state when it cools down to room temperature. Its permeability is now not much above that of air. The physical properties of the alloy differ in the two states. In the magnetic state its specific electrical resistance is 0.00052, while in the non-magnetic state it is .00072. Similar data for specific gravity are 7.98 and 8.15, and for tensile strength 135 and 80 kg. per sq. mm.

Photographs of the lines formed by the rays after reflection from the alloy are not alike, the number of lines being greater for the magnetic state. All of the lines for the non-magnetic state appear also for the magnetic state. The author interprets this to mean that upon the transition from the non-magnetic to the magnetic state there is a large increase in the number of atomic configurations of a certain kind which were present to only a small extent in the former condition.

G. F. S.



**An Analogy between Electrical Waves and X-rays.** N. KAPZOV. (*Ann. d. Physik*, No. 18, 1922.)—About a third of a century ago, when Hertz's demonstration of the actual existence of those electrical waves predicted by Maxwell, was still so recent that the wonder of it was still undulled by familiarity, it was no uncommon experience to meet in the periodical literature of physics some new proof that the new waves comported themselves in the same manner as light waves. Their reflection, refraction and interference were thus established. Then came the discovery of the X-rays and the battle between the conflicting views as to their nature. It is now known that they are light waves of extremely short length. For a long time it seemed impossible to reflect them from a surface. Now it is known that the surface of a crystal does this, and does it because within it are arranged layer after layer of atoms and electrons in regular order, though in fact diffraction is the real cause. This paper shows that the same effects are obtained when electrical waves enormous in comparison with X-rays are allowed to fall upon an artificial crystal. The elements are hollow copper cylinders, 12 mm. long and 3 mm. in diameter. Several of these are hung at equal intervals on a vertical thread. A sheet is formed by placing many such threads in the same plane and, finally, the crystal is made by placing several sheets parallel to one another and at equal distances. The electrical waves are of wave-length 3.5 cm. The cylinders act as resonators for the electrical waves.

When a bundle of electrical waves falls on the artificial crystal a reflected wave results and the intensity of this is measured as the crystal rotates, thus changing the angle of incidence. As the crystal turns the intensity of the reflected wave passes through maxima and minima, just as is the case with X-rays reflected from a natural crystal. More than this, when the positions of the crystal for maximum and minimum reflections are observed and the X-ray formula for the wave-length is applied, the result of the calculation is 3.2 cm. This may seem not sufficiently close to the value already given, 3.5 cm. When, however, the length of the waves was measured in the beam reflected from the crystal it was found to be 3.2 cm. Thus the two methods give concordant results. By some resonance effect the cylinders make the length of the reflected wave less than that of the incident wave.

The reflection was studied with one, then with two sheets and so on. The addition of the second sheet to the first caused a notable increase in the strength of the reflected ray, the third sheet produced a smaller increase and the presence of more sheets scarcely had any effect.

It is of interest that this very important work was done in the laboratory of the University of Moscow.

G. F. S.



NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

THE SO-CALLED HABITUATION TO "ARSENIC": VARIATION  
IN THE TOXICITY OF ARSENIOS OXIDE.<sup>1</sup>

By Erich W. Schwartz.

[ABSTRACT.]

THE toxicity of undissolved arsenious oxide varies markedly according to the fineness of its subdivision. Slight differences in toxicity of dissolved arsenious oxide are observed in different species of animals. The proportional differences are not always found when undissolved arsenious oxide is used. The behavior of undissolved arsenious oxide in the alimentary canal appears to be superimposed upon the species reaction to the dissolved arsenious oxide. Chickens presumably convert a coarse preparation into a fine one in their gizzards, so that the differences between coarse and fine preparations are here less marked than those found in the mammals tested. These results correlate a mass of acute toxicological data which heretofore have led to controversy and apparently contradictory evidence. Large doses of certain preparations of undissolved arsenious oxide and sulphide were recovered practically intact by washing and sieving the faeces.

The literature upon the subject of habituation to "arsenic" has been reviewed in the light of the data secured by the Bureau of Chemistry. No unimpeachable evidence exists that either man or other higher animals can acquire a tolerance to this drug, owing chiefly to the erroneous assumption that all preparations of undissolved arsenious oxide possess equal potency, and approach in degree the potency of dissolved arsenious oxide. The consumption of large amounts of undissolved arsenious oxide can be as readily explained on the basis that a relatively insoluble and coarse preparation was used as by assuming that habituation had been produced. The toleration of large doses may therefore be due not to an attribute inherent in the consumer, but to an attribute inherent in the preparation used, namely, its relative insolubility due to the relatively small extent of exposed surface of the particles and the low specific rate of solution.

---

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *J. Pharmacol.*, 20, Oct., 1922, 181.



**QUANTITATIVE DETERMINATION OF ANTHRAQUINONE.<sup>2</sup>**

By O. A. Nelson and C. E. Senseman.

[ABSTRACT.]

A METHOD has been developed by which anthraquinone may be determined quantitatively in mixtures containing also phenanthraquinone, anthracene, phenanthrene, phthalic anhydride, phthalic acid, or other oxidation products of anthracene or phenanthrene. It consists essentially in reducing the anthraquinone to the red oxanthranol, using zinc powder and 5 per cent. solution of sodium hydroxide. The red solution is filtered in vacuum and titrated with standard potassium permanganate.

**THE PREPARATION OF PHENYLGLYCINE-O-CARBOXYLIC ACID. I. FROM ANTHRANILIC ACID AND MONO-CHLORACETIC ACID.<sup>3</sup>**

By Herbert L. Haller.

[ABSTRACT.]

A STUDY of the preparation of phenylglycine-o-carboxylic acid from anthranilic acid and monochloroacetic acid has been undertaken. Optimum conditions have been determined for (1) concentration in water of the reacting substances, (2) time allowed for reaction, (3) ratio of reacting materials, (4) condensing agent, and (5) temperature of reaction mixture.

**Pure Ozone.**—SEBASTIAN KARRER and OLIVER R. WULF (*Jour. Amer. Chem. Soc.*, 1922, xlv, 2391-2397) prepared pure ozone by the fractional distillation of oxygen, which had been ozonized, then liquefied. The molecular weight of the pure ozone was determined by a vapor density method and found to be 47.3. The fact that the molecular weight is slightly lower than 48 is attributed to the presence of a small amount of oxygen. J. S. H.

**Pure Picric Acid.**—STANLEY R. BENEDICT, of Cornell University Medical College (*Jour. Biol. Chem.*, 1922, liv, 239-241), describes the preparation of picric acid of a high degree of purity by recrystallization of the technical grade of commercial picric acid from hot benzene. Since the solution of picric acid in benzene is highly inflammable, electric heating apparatus is used. The product obtained by this process is so pure that it may be used as a reagent in certain colorimetric determinations, such as that of creatinine. J. S. H.

<sup>2</sup> Published in *J. Ind. Eng. Chem.*, 14, Oct., 1922, 956.<sup>3</sup> Published in *J. Ind. Eng. Chem.*, 14, Nov., 1922, 1040.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

### THE PRODUCTION OF CARBON-BLACK FROM NATURAL GAS BY THE HIGH VOLTAGE ARC.

By J. J. Jakowsky.

THE legislation in many States against the present method of producing carbon-black by the incomplete combustion of natural gas, and the continually increasing demand for gas for other purposes, indicate that the supply of carbon-black may gradually be decreased and that new methods for its production, utilizing a greater percentage of the carbon in the gas should be developed. In the course of investigations of the effects on hydrocarbons of high voltage discharges, it was noted that under certain conditions natural gas could be decomposed and that carbon-black could be produced.

The effects of several types of electrical discharges on natural gas have, accordingly, been studied in order to find out the fundamental factors underlying the reactions and their possible influence in the recovery of a greater part of the carbon content of natural gas than is now possible. Present commercial plants using natural gas for the manufacture of carbon-black recover from 0.8 to 1.5 pounds of carbon-black per thousand cubic feet of gas consumed, or less than 5 per cent. of the total carbon in the gas. It should be noted, however, that the present methods involve heating the gas to incandescence by burning it as a luminous flame, and a considerable part of the gas is thus consumed as a source of heat. If this heat can be supplied from some other source, or if a more efficient method of applying the energy contained in part of the gas, to the decomposition of the rest of it, can be worked out, then a greater yield of carbon-black per thousand cubic feet of gas can be expected. Results showed that electrical production of carbon-black is a promising field, but further research is necessary to determine its commercial feasibility. Further details on the experiments are given in Serial No. 2417, recently published by the Bureau.

---

\* Communicated by the Director.



**GOLD IN OIL SHALES AND ITS POSSIBLE RECOVERY.**

**By Thomas Varley.**

STATEMENTS have appeared in the technical press, indicating that valuable metals such as gold, silver, platinum, and other rare metals, have been found and also have been successfully extracted from oil shales. An investigation of the subject was made by the metallurgical division of the Bureau of Mines, in order, if possible, to determine to what extent, if any, metals of value do occur in oil shales, and if so, the feasibility of attempting their recovery by the processes said to have been used for that purpose. An agreement was entered into with the owner of an extensive oil shale deposit in Wyoming, whereby I personally collected the samples of shales for use in the investigation.

The samples tested contained minute amounts of gold, to the extent of possibly 40 or 50 cents per ton of original shale, but the amount found is not of commercial value.

No special precautions are necessary in assaying shale for gold, any direct assay by a reliable method will give the true gold content of the original material. Further details will be found in Serial No. 2413, recently published by the Bureau.

---

**PREPARATION OF LIGHT ALUMINUM-COPPER  
CASTING ALLOYS.**

**By R. J. Anderson.**

IN aluminum-alloy foundry practice, light aluminum-copper alloys are preferred for general use for castings, in fact, as far as can be estimated from the available figures, the domestic production of castings from an alloy containing approximately 92 per cent. of aluminum and 8 per cent. of copper was about 97 per cent. of the castings in all kinds of alloys in 1920, which amounted to about 81,000,000 pounds. Several other binary aluminum-copper alloys are employed for commercial castings; these contain from 2 to 13.5 per cent. of copper, the remainder being aluminum. In the United States, the alloy containing 92:8 aluminum is regarded as the best alloy available for general casting purposes and for some special castings. In addition, more or less definite light alloys have been developed for particular uses, notably piston and carburetor alloys and alloys for so-called leak-proof parts.



Aluminum-alloy foundries in the United States employ three methods for introducing copper into aluminum in making light aluminum-copper alloys: (1) The use of copper directly; (2) the use of 33:67 copper-aluminum alloy; and (3) the use of 50:50 copper-aluminum alloy. The usual method of preparing rich alloys is to melt the copper and part of the aluminum separately and then to pour the copper into the aluminum, keeping the temperature as low as possible by adding the remainder of the cold aluminum. Experiments of the Bureau of Mines in the preparation of the rich alloys and No. 12 alloy have yielded data with regard to dross losses, relative costs, and merits of methods. Further details will be found in Technical Paper 287, of the Bureau of Mines.

---

**On the Selective Absorption of Electric Waves in Dielectrics.** W. ROMANOFF. (*Ann. d. Physik*, No. 18, 1922.)—Whatever is related to the nexus between matter and radiation may throw light on the structure of matter. The most thorough investigation of radiation and absorption has been made for the wave-lengths of the visible spectrum and the adjacent fields of the infra-red and ultra-violet; the territory of the X-rays is now under examination. It is in the range of the electric waves that the greatest gap in our knowledge of this subject exists.

A very simple method is here presented for studying the absorption of electric waves by liquids. A train of waves is set up along two wires. About 4 milligrams of liquid in a tube of fused quartz is placed where experiment has shown that it will not unduly disturb the electrical relations of the system. As the liquid absorbs the waves its temperature rises. This is measured by a thermal junction. A second thermo-element measures the electrical energy falling on the liquid. The ratio of the energy absorbed to the energy incident characterizes the absorptive power of the liquid for the wave-length employed. This method gives only relative results but it has the merit of convenience. Several of the alcohols were thus investigated. In general for the range of wave-lengths applied, 570 to 880 mm., the absorption ratio grows less as the wave-length increases. In isobutyl alcohol the ratio has a maximum value at the wave-length of 600 mm. For ethyl alcohol the ratio is four times as great for a wave-length of 570 mm. as for one of 880 mm. Selective absorption is thus shown to exist in all the alcohols examined.

G. F. S.

**The German Dye Industry.**—The leading nations involved against Germany were especially aroused during the war concerning the establishment of plants for manufacturing the synthetic coal-tar products, of which the dyes constitute the most important portion.



For many years Germany had practical control of the output of dyes, a condition due largely to the thorough coöperation of theory and practise, also to ingenious trade arrangements as to domestic distribution and export. The sudden stoppage of the supply became world-wide, for the Allies, of course, discontinued all commercial relations with their enemy, and the British blockade cut off supply to neutral countries. The several nations thus deprived proceeded to establish industries, and, after much difficulty and not a few failures, some of them have succeeded in producing many dyes and other synthetic tar products equal to those formerly manufactured only beyond the Rhine. Two methods have been employed as financial aids to these industries: Embargo on importation and high duty. Shortly after the Armistice, an embargo was placed by the U. S. Government on all dyes, except such as were not obtainable at reasonable price and satisfactory quality in the domestic market. This embargo has now been succeeded by the Tariff Act lately approved. The *Commerce Monthly* for December (issued by the National Bank of Commerce, New York) gives figures for the imports and domestic production of dyes, in pre-war and post-war years.

In 1914, the United States produced about six and one-half million pounds and imported nearly forty-six million pounds. In 1921, the figures are: Domestic production forty million pounds; importations somewhat less than four millions. In 1920, the domestic production was more than double that of 1921, but the result was large excess stock, which together with the industrial depression caused a material falling off in manufacture. It seems from the data at hand that the three great nations that were at war with Germany have succeeded in establishing satisfactory methods of making the more important dyes, but that these industries are still "infants" in the economic sense, and can only be maintained against German competition by embargo or tariff. Italy has employed the embargo method to prevent competition, but it has been for many years under German influence. The advertisements in Italian trade and scientific journals show that a very active propaganda is being carried on by German firms, and it will not be surprising if this newly developed industry is upset.

The problem is still more complicated by the fact there are large areas in which no such industry has been established, occupied by dense population who have demands for large amounts of dyes. Recent statistics show that Germany is now furnishing to China, Japan, Czechoslovakia, the Baltic States, and Austria large amounts of dyes. Germany's opportunities in some markets are materially increased by the monetary conditions. Since Germany's exchange is more nearly to the level of the exchanges of the markets of the Far East, the German manufacturer has an advantage over those in countries in which exchange is nearer par. All the data that come to us from Germany indicate that the Allied and Associated Powers have "scotched the snake, not killed it."

H. L.



# THE FRANKLIN INSTITUTE.

---

*(Proceedings of the Stated Meeting held Wednesday, December 20, 1922.)*

HALL OF THE FRANKLIN INSTITUTE,  
PHILADELPHIA, December 20, 1922.

DR. WALTON CLARK, President, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of:

Allen Addicks, Esq., B.S., Engineer, 106 South 36th Street, Philadelphia, Pennsylvania.

Francis L. Cramp, Esq., Assistant to President, Cramp's Shipyard, Philadelphia, Pennsylvania.

George C. Kuesel, Esq., D.D.S., Consulting Dental Surgeon, 1614 Locust Street, Philadelphia, Pennsylvania.

C. E. Kenneth Mees, Esq., D.Sc., Director, Research Laboratory, Eastman Kodak Company, Rochester, New York.

Joseph MacGregor Mitcheson, Esq., Assistant City Solicitor, 1018 Stock Exchange Building, Philadelphia, Pennsylvania.

Richard G. Sagebeer, Esq., B.A., Teacher, Haverford College, Haverford, Pennsylvania.

J. E. Shrader, Esq., Ph.D., Professor of Physics, Drexel Institute, Philadelphia, Pennsylvania.

Rodney H. True, Esq., Ph.D., Professor of Botany, University of Pennsylvania, Philadelphia, Pennsylvania.

William C. Tuttle, Esq., Manager of Trust Investments, Girard Trust Company, Broad and Chestnut Streets, Philadelphia, Pennsylvania.

Charles A. Williams, Esq., Chemist, 119 N. College Avenue, Oxford, Ohio; lectures before the Sections as follows:

"Recent Aeronautic Investigations and the Airplane Industry," by

Joseph S. Ames, Ph.D., LL.D.,

Professor of Physics,

The Johns Hopkins University,

Baltimore, Maryland;

"Recent Advances in Photographic Theory," by

C. E. Kenneth Mees, D.Sc., Director,

Research Laboratory,

Eastman Kodak Company,

Rochester, New York;



"The Earliest Apparatus and Procedures of Photography: Contributions to the Centenary of Modern Photographic Methods," by

Henry Leffmann, A.M., M.D.,

Lecturer on Research,

Philadelphia College of Pharmacy and Science,

Philadelphia, Pennsylvania;

and a lecture before the Stated Meeting November 15, 1922, by

E. Newton Harvey, Ph.D.,

Professor of Physiology,

Princeton University,

Princeton, New Jersey,

on "Animal Luminescence";

also additions to the library by gift, 83 volumes and 209 pamphlets; by purchase, 11 volumes and 1 pamphlet.

The Committee on Nominations appointed by Vice-President Henry Howson in accordance with a resolution passed at the Stated Meeting, held November fifteenth last, presented the following list of nominees to be voted for at the annual election to be held on Wednesday, January 17, 1923:

For President (to serve one year), Walton Clark.

For Vice-President (to serve three years), W. C. L. Eglin.

For Treasurer (to serve one year), Benjamin Franklin.

For Managers (to serve three years), Gellert Alleman, G. H. Clamer, Theobald F. Clark, Walton Forstall, Benjamin Franklin, Harry F. Keller, George D. Rosengarten, Wm. Chattin Wetherill; (to serve two years), J. T. Wallis; (to serve one year), J. Bartleman Klumpp.

On motion, duly seconded, the nominations were closed.

The Chairman then recognized Dr. Thomas D. Cope, who introduced Dr. A. H. Pfund of The Johns Hopkins University, Baltimore, Maryland, who had recently been awarded the Edward Longstreth Medal for his Cryptometer, Paint Film Gauge, Colorimeter and Rotating Sector.

Doctor Cope said, "Mr. President, Members of the Institute, Ladies and Gentlemen: Some time ago our medalist, Doctor Pfund, was called upon to apply in the paint industry the knowledge which he had acquired as a physicist while working upon the problems which he had met in his laboratory. He has left his mark upon the paint industry in the form of four instruments, the Cryptometer, the Paint Film Gauge, a Colorimeter for nearly white surfaces, and a Precision Rotating Sector. The Cryptometer is an instrument for determining the area which one gallon of white or black paint will conceal. The Paint Film Gauge permits a rapid determination of the thickness of a film of wet paint. The Colorimeter enables the deviation from true white of a nearly white surface to be determined both qualitatively and quantitatively. The Precision Rotating Sector enables the observer to determine the angular opening of a sector while the sector is in rapid rotation. The essential feature of this instrument is a simple and elegant optical device.

"These instruments have been thoroughly investigated by the Committee on Science and the Arts. They have been found sound in principle, well designed and well adapted to meet the problems which they are intended to solve. The Committee finds, too, that these instruments are in extensive use



and are looked upon by their users as important contributions to the art of precise measurement in the paint industry. In recognition of the originality and ingenuity displayed by Doctor Pfund in designing these instruments by means of which he has introduced physical methods of precision into the paint industry, the Institute acting on the recommendation of the Committee on Science and the Arts has awarded to him the Edward Longstreth Medal of Merit.

"I have the honour, Mr. President, to present to you Dr. A. H. Pfund, Associate Professor of Physics at Johns Hopkins University, Baltimore, Maryland."

The Chairman then presented the Medal, Certificate and Report to Doctor Pfund, who in accepting them said:

"*Mr. President:* This is an honor, indeed, to be thus recognized by The Franklin Institute. I accept this medal gratefully and in all humility.

"The work for which the present award was made lies in the field of applied science. It is often thought that this field is a borrower only—taking the ideas and discoveries of pure science and making them useful to man. This is a mistake. Practical things, be they products or processes, bring about new conditions which, in turn, unearth new problems. These problems, if pursued to their logical conclusion, inspire research of the purest and loftiest type.

"Thus is a reciprocity established which aids in the furtherance of both fields of endeavor."

The paper of the evening was then presented by Dr. W. F. G. Swann, Professor of Physics, University of Minnesota, Minneapolis, Minnesota, on "Unsolved Problems of Cosmical Physics." The status of our knowledge of the earth's magnetic and electric phenomena was discussed as well as the origins of magnetic storms, earth-currents, the aurora borealis and their relations to the sun's activity. Consideration was also given to the modern views of the origin of gravitation and the bearing of Einstein's theory upon gravitational phenomena. The subject was illustrated by lantern slides.

A unanimous vote of thanks was extended to the speaker.

Adjourned.

R. B. OWENS.  
*Secretary.*

---

## COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday,  
December 6, 1922.)*

HALL OF THE INSTITUTE,  
PHILADELPHIA, December 6, 1922.

DR. JAMES BARNES *in the Chair.*

The following reports were presented for final action:



No. 2793: Cryptometer, Colorimeter, Paint Film Gauge and Rotating Sector. The Edward Longstreth Medal to Dr. A. H. Pfund of Baltimore, Maryland.

No. 2795: Johnson Hydraulic Valve. The Elliott Cresson Medal to Mr. Raymond D. Johnson of New York.

The following reports were presented for first reading:

No. 2801 }  
and } The Franklin Medal.  
No. 2802 }

R. B. OWENS,  
*Secretary.*

---

## SECTIONS.

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 9, 1922, at eight o'clock, with Dr. Harry F. Keller in the Chair. The minutes of the previous meeting were read and approved.

Wilder D. Bancroft, Ph.D., World War Memorial Professor of Physical Chemistry in Cornell University, Ithaca, New York, presented a communication on "Structural Colors in Feathers." These conclusions were drawn: Reds, yellows and blacks are pigment colors; whites, blues, greens, and the metallic colors are structural colors; the metallic colors are interference colors, due to thin films.

The paper was discussed; a vote of thanks was extended to Doctor Bancroft; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 23, 1922, at eight o'clock, with Dr. Thomas D. Cope in the Chair. The minutes of the previous meeting were read and approved.

Joseph S. Ames, Ph.D., LL.D., Professor of Physics at The Johns Hopkins University and Director of the Office of Aeronautical Intelligence, National Advisory Committee for Aeronautics, presented a communication entitled, "Recent Aeronautic Investigations and the Airplane Industry." A description was given of (a) the distribution of forces over the various surfaces of an airplane, (b) the motion of the airplane in manœuvres, and (c) the study of the scale effect in aerodynamics. The immediate application of experimental researches in the airplane industry was discussed.

The communication was discussed; a vote of thanks was extended to Doctor Ames; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*



*Section of Physics and Chemistry and Section of Photography and Microscopy.*—A joint meeting of the Sections was held in the Hall of the Institute on Thursday evening, December 7, 1922, at eight o'clock, with Dr. H. J. M. Creighton in the Chair. The minutes of the previous meeting were approved as published.

C. E. Kenneth Mees, Sc.D., Director of the Research Laboratory, Eastman Kodak Company, Rochester, New York, delivered a lecture on "Recent Advances in Photographic Theory," in which a resumé was given of the recent researches in this field.

The lecture was illustrated by means of lantern slides. The communication was discussed; a vote of thanks was extended to Doctor Mees; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

*Section of Physics and Chemistry and Section of Photography and Microscopy.*—A joint meeting of the Sections was held in the Hall of the Institute on Thursday evening, December 14, 1922, at eight o'clock, with Mr. Alfred Rigling in the Chair. The minutes of the previous meeting were read and approved.

Henry Leffmann, A.M., M.D., Ph.D., Lecturer on Research in the Philadelphia College of Pharmacy and Science, delivered a lecture on "The Earliest Apparatus and Procedures of Photography: Contributions to the Centenary of Modern Photographic Methods." The work of Niépce, and other investigators prior to Daguerre, concerning the action of light on various substances was reviewed; and the types of camera and the technic used by these early investigators were described. The lecture was illustrated by means of experiments and lantern slides.

The paper was discussed; a vote of thanks was extended to Doctor Leffmann; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

---

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, December 13, 1922.)*

#### RESIDENT MEMBERS.

- MR. FRANCIS L. CRAMP, Cramp's Shipyard, Richmond and Norris Streets, Philadelphia, Pennsylvania.  
DR. GEORGE C. KUESEL, 1614 Locust Street, Philadelphia, Pennsylvania.  
MR. JOSEPH MACGREGOR MITCHESON, 1018 Stock Exchange Building, Philadelphia, Pennsylvania.  
MR. RICHARD G. SAGEBEER, Harverford College, Haverford, Pennsylvania.  
DR. J. E. SHRADER, Drexel Institute, Philadelphia, Pennsylvania.  
DR. RODNEY H. TRUE, Department of Botany, University of Pennsylvania, Philadelphia, Pennsylvania.



MR. WILLIAM C. TUTTLE, Girard Trust Company, Philadelphia, Pennsylvania.  
MR. CHARLES A. WILLIAMS, 917 Madison Street, Chester, Pennsylvania.

## NON-RESIDENT.

DR. C. E. K. MEES, Director, Research Laboratory, Eastman Kodak Company,  
Rochester, New York.

## ASSOCIATE.

MR. ALLEN ADDICKS, 106 South 36th Street, Philadelphia, Pennsylvania.

## CHANGES OF ADDRESS.

MR. WALTER ATLEE, 218 East Twentieth Street, Baltimore, Maryland.  
MR. GEORGE W. BIRCH, JR., 19 Fairview Avenue, Highland Park, Pennsylvania.  
MR. JOHN STUART EASON, 522 Merchants Bank Building, St. Paul, Minnesota.  
MR. HERMAN LIVINGSTON, Richards Park, Somerville, New Jersey.  
MR. JOHN C. TRAUTWINE, 3rd, Morton Avenue and Providence Road, Morton,  
Pennsylvania.  
MR. H. R. VAN DEVENTER, Dubilier Condenser and Radio Corporation, 48  
West Fourth Street, New York City, New York.  
MR. J. M. WEISS, 210 West 110th Street, New York City, New York.

NECROLOGY.

**John Forrest Kelly** was born in Carrick-on-Suir, Ireland, March 28, 1859, and died at Pittsfield, Massachusetts, on October 15, 1922. He came to the United States when a boy and graduated from Stevens Institute of Technology in 1878 with the degree of Bachelor of Science, the degree of Doctor of Philosophy being conferred upon him three years later by the same institution. In 1879 he entered the Edison Laboratory as a chemist, and later joined the staff of the Western Electric Company. During the following twenty-five years he acted as technical advisor to many important electrical interests. More than ninety patents were granted to Doctor Kelly for devices used in the generation, distribution, transmission and measurement of electrical power and energy. In 1895, he founded the Tel-Electric Company. In 1910, on the recommendation of The Franklin Institute, the City of Philadelphia awarded him the John Scott Legacy Medal and Premium for his electric piano player. In recent years, Doctor Kelly had been interested in processes for the drying of food products.

Doctor Kelly was a member of the leading scientific and technical societies of the United States and Europe. He became a member of The Franklin Institute on April 12, 1913.

**Mr. John E. Carter**, 5356 Knox Street, Germantown, Philadelphia, Pennsylvania.

**Rear Admiral John R. Edwards**, Bristol, Rhode Island.

**Mr. John Wanamaker**, 1300 Market Street, Philadelphia, Pennsylvania.



## LIBRARY NOTES.

## PURCHASES.

- ADVISORY COMMITTEE FOR AERONAUTICS.—Report of the Light Alloys Subcommittee. 1921.
- CROSS, C. F., and DORÉE, C.—Researches on Cellulose, vol. 4, 1910-21. 1922.
- GANSWINDT, A.—Dyeing Silk, Mixed Silk Fabrics and Artificial Silks. Tr. by Charles Salter. 1921.
- MARTIN, T. C., and COLES, S. L.—Story of Electricity, vol. 2. 1922.
- NATIONAL ASSOCIATION OF COTTON MANUFACTURERS.—Year Book and Manual. 1922.
- Newcomen Society for the Study of the History of Engineering and Technology, Transactions, vol. 1, 1920-21. 1922.
- Physical Society of London and the Optical Society.—Discussion on the Making of Reflecting Surfaces. No date.
- PLIMMER, R. H. A.—Analyses and Energy Values of Foods. 1921.
- Royal Society of Edinburgh, Transactions 1921-22, vol. 53, Pt. 1. 1922.
- SABATIER, P.—Catalysis in Organic Chemistry. Tr. by E. Emmet Reid. 1922.
- SMITS, A.—Theory of Allotropy. Tr. by J. Smeath Thomas. 1922.
- STILLMAN, J. M.—Paracelsus. 1920.
- TUTTLE, J. B.—Analysis of Rubber. 1922.

## GIFTS.

- Allen Cone Company, Bulletin No. 23, Allen Sand Tank. El Paso, Texas, 1922. (From the Company.)
- American Society of Heating and Ventilating Engineers, Year Book 1922. New York City, New York, 1922. (From the Society.)
- Association of Iron and Steel Electrical Engineers, Proceedings, 1921. Pittsburgh, Pennsylvania, no date. (From the Association.)
- Australasian Association for the Advancement of Science, Report of the Fifteenth Meeting, January, 1921. Melbourne, Australia, 1921. (From the Association.)
- Barber Asphalt Company, The Last Analysis and the Wonderland of Trinidad. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Brown Instrument Company, Catalogue No. 85, Brown Automatic Control Signalling and Alarm Instruments. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Bruntons, Splicing and Socketing of Wire Ropes. Musselburgh, Scotland, 1922. (From the Company.)
- Calkins Company, Catalogue H, "Calkins" Specialties. Los Angeles, California, 1922. (From the Company.)
- Cambridge and Paul Instrument Company, Limited, Lists of Instruments, Pyrometers and Thermometers Nos. 100, 157, 161, 164, 165, 190, 191, 194, and 195A. London, England, 1922. (From the Company.)
- Canada Department of the Interior, Irrigation Series, Bulletin No. 6, Irrigation Practice and Water Requirements for Crops in Alberta. Ottawa, Canada, 1922. (From the Department.)
- Canada Department of Mines, Talc and Soapstone in Canada by Hugh S. Spence. Ottawa, Canada, 1922. (From the Department.)



- Canadian Car and Foundry Company, Limited, Bulletins Nos. T2 and S5. Montreal, Canada, 1921. (From the Company.)
- Carborundum Company, Booklet of Carborundum Anti-slip Tile. Niagara Falls, New York, 1922. (From the Company.)
- Climax Engineering Company, Bulletin 1001. Clinton, Iowa, 1922. (From the Company.)
- Century Electric Company, Bulletins Nos. 28, 29, 30 and 31. St. Louis, Missouri, 1922. (From the Company.)
- Coeur d'Alene Hardware and Foundry Company, Bulletin No. 21. Wallace, Idaho, 1922. (From the Company.)
- Colorado State Bureau of Mines, Annual Report for the Year 1921. Denver, Colorado, 1922. (From the Bureau.)
- Connecticut State Geological and Natural History Survey, Bulletins 23 to 32 inclusive. Hartford, Connecticut, 1920. (From the State Geologist.)
- Connersville Blower Company, Bulletin No. 4, Rotary Displacement Meters. Connersville, Indiana, 1922. (From the Company.)
- Consolidated Pneumatic Tool Company, Limited, Electric Tool Catalogue. London, England, 1922. (From the Company.)
- Constantinesco, George, Theory of Wave Transmission and Pamphlet on Wave Transmission. London, England, 1922. (From Mr. Walter Haddon.)
- Continental Radio and Electric Corporation, Modern Radio 1922. New York City, New York, 1922. (From the Corporation.)
- Crouse-Hinds Company, Catalogue No. 2000, Condulets. Syracuse, New York, 1922. (From the Company.)
- Cunard Steamship Company, Limited, Over Eighty Years of Trans-Atlantic Travel and Atlas of the World. New York City, New York, 1922. (From the Company.)
- Dayton-Dowd Company, Booklet on Centrifugal Pumps. Quincy, Illinois, 1922. (From the Company.)
- Dixon Valve and Coupling Company, Catalogue No. 6. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Dust Recovering and Conveying Company, Bulletin No. 5. Cleveland, Ohio, 1922. (From the Company.)
- Electric Storage Battery Company, Binder containing a Complete Set of Bulletins, Form 1296 and two booklets "Facts." Philadelphia, Pennsylvania, 1922. (From the Company.)
- Engineer Company, Turner Baffle Book. New York City, New York, 1922. (From the Company.)
- Falk Corporation, Bulletins Nos. 31 and 32, Herringbone Gears. Milwaukee, Wisconsin, 1922. (From the Corporation.)
- Fall River Water Works, Report of the Watuppa Water Board. Fall River, Massachusetts, 1922. (From the Works.)
- Federal Telephone and Telegraph Company, Bulletin No. 119-W. Buffalo, New York, 1922. (From the Company.)
- Georgetown University, Triennial Report of the Extra-curriculum Activities of Georgetown University. Washington, District of Columbia, 1922. (From the University.)



- Gifford-Wood Company, Catalogue No. 64. Hudson, New York, 1922. (From the Company.)
- Goodall Rubber Company, Incorporated, Rubber Products and Semi-Metallic Hose. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Good Roads Machinery Company, Incorporated, Champion Crushing and Quarrying Machinery. Kennett Square, Pennsylvania, 1922. (From the Company.)
- Hayward Company, Catalogue No. 43 of Hayward Buckets. New York City, New York, 1922. (From the Company.)
- Ingersoll-Rand Company, Compressed Air for Trench, Tunnel and Pipe Work. New York City, New York, 1922. (From the Company.)
- Institution of Automobile Engineers, Proceedings, Session 1921-22, Part I. London, England, 1922. (From the Institution.)
- International Nickel Company, Pamphlet of Monel Metal and Nickel Products. New York City, New York, 1922. (From the Company.)
- International Western Electric Company, Electrical Communication, Vol. 1, No. 1. New York City, New York, 1922. (From the Company.)
- Iowa Engineering Society, Proceedings of the Thirty-fourth Annual Meeting. Des Moines, Iowa, 1922. (From the Society.)
- Jeffrey Manufacturing Company, Catalogues Nos. 277 and 368. Swing Hammer Pulverizers and Machinery for Fertilizer Plants. Columbus, Ohio, 1922. (From the Company.)
- Lea Recorder Company, Limited, Bulletin of Lea Coal Meters and Booklet M, A Book for Steam Users. Manchester, England, 1922. (From the Company.)
- Manila Bureau of Education, Twenty-second Annual Report of the Director of Education for 1921. Manila, Philippine Islands, 1922. (From the Bureau.)
- Marks, H. E., Corporation, Marks System of Gypsum Roofs. Pittsburgh, Pennsylvania, 1922. (From the Corporation.)
- Marshall Sons and Company, Limited, Steam Traction Engines. Gainsborough, Scotland, 1922. (From the Company.)
- Medart Company, Catalogue 43. St. Louis, Missouri, 1922. (From the Company.)
- Medford Water and Sewer Commissioners, Annual Report for the Year Ending December 31, 1921. Medford, Massachusetts, 1922. (From the Commissioners.)
- Mellon Institute of Industrial Research, Recent Progress in Smoke Abatement and Fuel Technology in England and Bibliographic Series Bulletin No. 1. Pittsburgh, Pennsylvania, 1922. (From the Institute.)
- National Physical Laboratory of Teddington, Report for the Year 1921 and Collected Researches, Vol. xvi, 1921. London, England, 1921. (From the Laboratory.)
- New Hampshire Public Service Commission, Reports and Orders, Advance Sheet No. 7, Vol. viii. Concord, New Hampshire, 1922. (From the Commissioners.)
- Nobel Industries, Limited, Metal Breaking with Explosives. London, England, 1922. (From the Company.)



- Ohio Geological Survey, Bulletin 25, Pottsville Fauna of Ohio by Helen Morningstar. Columbus, Ohio, 1922. (From the State Geologist.)
- Ohio Hydrate and Supply Company, A Job That Took a Million Years or The Tale of the Clam. Woodville, Ohio, 1922. (From the Company.)
- Ontario Department of Agriculture, Bulletins 289 and 290, Sixteenth Annual Report of the Horticultural Societies for the Year 1921, and Report of the Women's Institutes of the Province of Ontario, 1920 and 1921. Toronto, Canada, 1922. (From the Department.)
- Philadelphia Rapid Transit Company, Souvenir Booklet Giving a Brief Account of the Construction, Equipment and Operating Agreement of the Frankford Elevated Railway and Bustleton Surface Line. Philadelphia, Pennsylvania, 1922. (From Mr. John J. L. Houston.)
- Pike Manufacturing Company, Sharpening Stones and Abrasive Specialties. Pike, New Hampshire, 1922. (From the Company.)
- Portland Commission of Public Docks, The Port of Portland. Portland, Oregon, 1922. (From the Commissioners.)
- Power Manufacturing Company, Primm Oil Engines. Marion, Ohio, 1922. (From the Company.)
- Public Ledger Company, Philadelphia, Historic, Central Metropolitan and Industrial. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Radio Corporation of America, Pamphlets, Radio of To-day and Tomorrow, How to Send a Radiogram and Radio Central, World-wide Wireless. New York City, New York, 1922. (From the Corporation.)
- Royal Dublin Society, Scientific Proceedings, Vol. xvi, Nos. 35-39, and Vol. xvii, Nos. 1-10. Dublin, Ireland, 1922. (From the Society.)
- Sanderson Bibby Company, Limited, High Efficiency Mill Gearing. London, England, 1922. (From the Company.)
- Smith, Edgar F., Franklin Bache, Chemist. Philadelphia, Pennsylvania, 1922. (From the Author.)
- Smithsonian Institution, New Timeline Birds from the East Indies, Publication No. 2674. Washington, District of Columbia, 1922. (From the Institution.)
- Southern Pine Association, Southern Pine, What It Is and What It Is Used For. New Orleans, Louisiana, 1922. (From the Association.)
- Stanford University, Biological Sciences Publications, Vol. ii, No. 3, and Vol. iii, No. 1. Stanford University, California, 1922. (From the University.)
- States Company, Electric Meter Testing Apparatus. Hartford, Connecticut, 1922. (From the Company.)
- Steam Power Publishing Company, Steam Power, February to September, 1922. Chicago, Illinois, 1922. (From the Company.)
- Stromberg Motor Devices Company, Essential Information for Car Owners and Stromberg Plain Tube Carburetor. Chicago, Illinois, 1922. (From the Company.)
- Sturtevant, B. F., Company, Catalogue No. 291 and Bulletin No. 296. Boston, Massachusetts, 1922. (From the Company.)
- Sullivan Machinery Company, Bulletins 70, 72, 74, 77 and 79. Chicago, Illinois, 1922. (From the Company.)
- Sweet's Catalogue Service, Sweet's Engineering Catalogue, Second Annual



- Edition. New York City, New York, 1915. (From Mr. John J. L. Houston.)
- Technische Hoogeschool, Delft, Holland, Seven Dissertations Presented during 1921 and Two Dissertations Presented during 1922. Delft, Holland. (From the High School.)
- Tyler, W. S., Company, Catalogue 50, Double Crimped Screen. Cleveland, Ohio, 1922. (From the Company.)
- United States Air Service, Information Circulars Nos. 303, 341, 354, 355, 357, 363, 364, 368, and 369. Washington, District of Columbia, 1922. (From the Chief of Air Service.)
- United States Bureau of Foreign and Domestic Commerce, Foreign Commerce and Navigation for 1921. Washington, District of Columbia, 1922. (From the Bureau.)
- United States Galvanizing and Plating Equipment Corporation, Bulletins 100 and 105. Brooklyn, New York, 1922. (From the Corporation.)
- United States Gypsum Company, How to Get Best Results from Gypsum Plaster. Chicago, Illinois, 1922. (From the Company.)
- University of Kansas, Annual Catalogue, Section I, General Information, Section II, Announcement of Courses, and Section III, Roster of Faculty, Students and Graduates. Topeka, Kansas, 1922. (From the University.)
- University of Pittsburgh, Publications of the Allegheny Observatory, Vol. 6, No. 5. Pittsburgh, Pennsylvania, 1922. (From the Observatory.)
- University of Virginia, Virginia Geological Survey Bulletin No. 23. Charlottesville, Virginia, 1922. (From the University.)
- University of Washington, Catalogue 1921-1922 and Announcements 1922-1923. Seattle, Washington, 1922. (From the University.)
- Wellington Census and Statistics Office, Report on the Justice Statistics, Vital Statistics and Statistical Report on the Population of the Dominion of New Zealand for the Year 1921. Wellington, New Zealand, 1922. (From the Census and Statistics Office.)
- Wing, L. J., Manufacturing Company, Bulletin 57, Wing Turbine Blowers. New York City, New York, 1922. (From the Company.)
- Wisconsin Directory Company, Stationary Engineers' Book 1910-1911. Milwaukee, Wisconsin, 1911. (From Mr. John J. L. Houston.)
- Wisconsin Geological and Natural History Survey, Bulletin 64, Inland Lakes of Wisconsin. Madison, Wisconsin, 1922. (From the State Geologist.)
- Wright Manufacturing Company, Catalogue No. 10. Lisbon, Ohio, 1922. (From the Company.)

---

## BOOK NOTICES.

CATALYSIS IN ORGANIC CHEMISTRY. By Paul Sabatier, Member of the Institute. Translated by E. Emmet Reid, Johns Hopkins University. xxiv-969 pages, pages with name and subject indexes, 8vo. New York, D. Van Nostrand Company. Price, \$5 net.

The term catalysis in its chemical application was introduced by Berzelius, but was in use in English, at least, as early as 1635, with the general meaning of catastrophe or dissolution. It was also used by Libavius.



Berzelius' application of it was first made in an article in the *Ann. d. Chim.* (1836, vol. 61, 150), in which he expressed his view as follows:

"This new force, which was unknown until now, is common to organic and inorganic nature. I do not think that it is a force wholly independent of the electrochemical affinities of matter; on the contrary, I think that it is only a new manifestation, but in so far as we can note the connection between them and their mutual relations, it will be appropriate to designate it by a distinct name. I will call it *catalytic force*, and will term *catalysis* the decomposition of substance by this force, analogous to our use of the term analysis for the decomposition of substances by chemical affinity."

It is interesting to note that four years before Berzelius published his paper, Döbereiner had discovered a striking instance of catalysis in the inorganic field, without, however, discussing the nature of action or assigning any title to it. This was the action of manganese dioxide in facilitating the decomposition of potassium chlorate. His report appeared in *Annalen* (1832, I, 236). It is a little surprising that the earliest use of the term catalysis by Berzelius is in Sabatier's work referred to his *Traité de Chimie* of 1845, whereas the date of his application of the term is, as noted above, nine years earlier.

Catalytic actions have been extensively studied and an immense number of instances is known. Many are of only theoretical interest, but many others again are of the greatest practical importance. The mechanism of the action is still in great measure obscure. Even the exact limitations of the phenomena are not absolutely fixed. Ostwald's definition has been in favor. It is "a catalyst is a substance which influences the velocity of a reaction without appearing in the final product." This would, as Sabatier remarks, greatly widen the extension of the term, for water has a very active power of increasing the velocity of reactions. The degree of fineness of powders is also influential. Strictly speaking the catalyst does appear in the final product, although not as part of the results of its action. Perhaps a better, though slightly more pedantic, definition is "a substance that modifies the specific velocity of a reaction without stoichiometric participation therein." The work in hand devotes considerable space to the mechanism of catalysis. A very interesting phase of the subject is the susceptibility of catalysts to interference by the presence of small amounts of other substances and also susceptibility to temperature and hydrogen-ion concentration. These latter influences have been especially noted in regard to the class of catalysts commonly termed "enzymes" or "non-organized ferments," the latter, however, a phrase that should be avoided. Diatase, invertase, pepsase, trypase and similar catalysts, that take such a great part in the processes of digestion in plants and animals, are very susceptible to temperature and to the reaction of the liquid. The susceptibility of many catalysts to interference by small amounts of other substances, generally called "poisoning," has been studied a great deal in connection with some industrial process. Thus, the contact method for sulphuric acid depends on the use of platinum in a finely divided condition, but the presence of some other metals, such as arsenic and mercury in very minute amounts, will soon render the platinum inert. Berliner has shown that the presence of fatty vapors in the air, or grease from the stops,



will decrease the absorption of hydrogen by palladium to practically zero. In this connection the work of Chaney, presented to the thirty-ninth general meeting of the American Electrochemical Society (1919) on the activation of charcoals, will be of value. It was shown that all primary amorphous carbon consists essentially of a stabilized complex of hydrocarbons adsorbed on a base of active carbon. Charcoals prepared at moderately high temperatures retain considerable amounts of hydrocarbons. A hydrocarbon resembling anthracene, boiling at  $360^{\circ}$  C., was isolated from cedar charcoal which had been calcined at  $850^{\circ}$  C., and chlorine substitutions may be obtained in notable quantity by passing chlorine over coconut or other charcoals which have been calcined at high temperatures.

As might be expected, a large space in the book is devoted to the procedures of hydrogenation, a field in which the author has been very actively engaged and in which he has been a pioneer. Outside of the chapters on hydrogenation, a large amount of data of various types is to be found, and the book shows how extensive and complicated is the field of catalytic action. Being limited to organic chemistry, many phases of the phenomenon are necessarily omitted, but it seems that the process for production of ammonia by direct union should have been included. It is true that the main object of the process as applied practically is to the manufacture of inorganic bodies, but ammonia and nitric acid have intimate relations with organic chemistry, and the Haber process has been so much discussed lately that it would have been interesting and useful to have the opinions of the author and translator concerning it, and concerning the cause of the terrific explosion at the Oppau plant. The translator has done well in the work of turning the French into English, and has also done an especial service in verifying the numerous references. We must also thank him cordially for having given two very full indexes—names and subjects—which were probably lacking in the original, as French scientists are notoriously and criminally negligent on that score. One point in the make-up of the book deserves unfavorable criticism. The text is divided into many brief paragraphs, and the index references are to these paragraphs. This, in itself, is not seriously objectionable, but the paging of the book is carried on the inside of each leaf, while the initial and final paragraph numbers are in the places usually occupied by the paging. There seems to be no necessity for this arrangement. It is certainly very unusual in American books, and it is to be hoped that the custom will not be followed. If the form is borrowed from the French original then we can say that there are some things which are not "ordered better in France."

HENRY LEFFMANN.

THE NEWCOMEN SOCIETY FOR THE STUDY OF THE HISTORY OF ENGINEERING AND TECHNOLOGY. Transactions, Vol. 1, 1920-21. 77 pages, official data and index, 18 plates, quarto form,  $7\frac{1}{2}$  by 10 in. Printed for the Society. Price 20 shillings.

The scope of the society is sufficiently indicated in its title. Although at present made up of British membership, it will be the endeavor of its promoters to make it international. It is believed to be the first society formed for its purpose. The plates are representations of early British inventions.



The initial article is by E. W. Hulme, B.A., entitled "An Introduction to the Literature of Historical Engineering to the Year 1640." It would seem to be better form to say "Historical Literature of Engineering," which is really what the author means, but this may be thought hypercriticism. The history of engineering, it appears, has its mysteries, for an article by L. St. L. Pendred is on "The Mystery of Trevithik's London Locomotives." The formation of the society and the appearance of the first volume of its Transactions are gratifying evidences of the spread of a broader culture among those whose labors are so strongly directed to the practical side of human affairs. Full information as to the terms and conditions of membership can be obtained by addressing the Hon. Secretary and Treasurer, H. W. Dickinson, M.I., Mech.E., The Science Museum, South Kensington, London, S. W. 7.

HENRY LEFFMANN.

THE PROPERTIES OF ELECTRICAL CONDUCTING SYSTEMS, INCLUDING ELECTROLYTES AND METALS. By Charles A. Kraus, Clark University. 408 pages, indexes and 70 illustrations, 8vo. New York, The Chemical Catalog Company, 1922. Price \$4.50 net.

This is another volume of the American Chemical Society's monograph series, and in form and style follows those previously issued. The series is intended to present special considerations of chemistry and physical chemistry, in a detail that is not possible in the ordinary text-book or dictionary. The volume in hand goes very deeply into the theories and practise of electrolysis, though not dealing directly with technologic phases. The enormous development of electricity in all fields is evident in many ways, and in this book we have the evidence of how vast has been the advance since Faraday announced his results on electrolytic effects. Professor Kraus states in the preface that the most recent developments of chemistry and molecular physics have been principally along the line of the application of the theory of ionization to our conception of matter. The primary views have passed away, as is the case with all early theories, but have served as a guide in directing and suggesting research. To-day an intimate relation between matter and electricity is accepted as a principle as securely established as the atomic theory itself. The theoretical interest and practical importance of electrolytic phenomena have been a powerful impulse towards experimenting along such lines, and hence the literature of chemistry and physics abounds with contributions purely theoretical and purely practical, as well as those which touch both fields. The successful establishment of the American Electrochemical Society is one of the indications of the extensive cultivation of this branch of science. The data that have been obtained by the many workers are scattered through many journals and transactions, and the purpose of the present volume is to summarize these contributions and thus make them easily available to the student or to research workers. The volume is also adapted to the wants of workers in allied branches.

Principal attention has been given to systems in which ionic phenomena are clearly in evidence. Metallic systems are included, as a relation between phenomena in metallic and electrolytic systems is unmistakeable. The subject of electrolytic solutions is the most extensively treated, and all data are



given from essentially an empirical standpoint, as the author holds that as yet an adequate theory of electrolytic solutions has not been brought forward. The theory finally adopted will, he thinks, be a composite and will embody some of the fundamental elements of the older ionic theory.

Many tables and diagrams are added, and the book constitutes a very comprehensive collection of data on a subject of great importance and much abstruseness. The numerous references to the literature enable the user of the book to fill out details along any line that may be in hand. The mechanical execution is excellent.

HENRY LEFFMANN.

THE RECOVERY OF VOLATILE SOLVENTS. By Clark Shove Robinson, Massachusetts Institute of Technology. 183 pages, index and 73 illustrations. 8vo. New York, The Chemical Catalog Company. Price \$2.50 net.

The term volatile solvents might be difficult to define, for water and mercury come within a broad interpretation thereof. The book in hand, of course, does not cover so wide a range, but relates to the familiar organic liquids that are used for extractions with substances that water does not appreciably dissolve. In the analytic laboratory the use of "miscible" and "immiscible" solvents is frequent, and here again a captious critic might challenge the accuracy of the phrase, for in strict construction, every so-called immiscible solvent dissolves to a certain extent in the other liquid—almost always water—and is also to a limited extent dissolved by it. The author gives, indeed, a rather wide interpretation to his title, but not in either of the directions just noted, descriptions being given of methods used for extracting gasoline from natural gas.

The recovery of volatile solvents has been long practised on a limited scale in the analytic and research laboratory, especially with the more expensive liquids, but the purpose of this work is to give the existing state of the art and theories as applied to large scale operations. The solvents used in the laboratory and even in industries in early days were few. Alcohol, ether, chloroform, light petroleum and light tar distillates were the familiar forms. The list in this book includes over two score substances, some of them moderately complicated synthetic products. The importance of accurate study of the physics and chemistry of solvent recovery lies principally in the cost of the material, but in some cases increasing scarcity is a dominant urge. Notwithstanding the fact that the present work is the first of its type that has appeared, the literature of the subject is very extensive. It is presented in excellent form in an appendix, the items being arranged chronologically. A considerable number of the items are records of patents, a fact that indicates the extensive development that the procedures have in industries. Scientists should interest themselves in securing some international and authoritative methods of quoting and arranging references. Two methods of arranging are in frequent use: Chronological and alphabetical, the latter by authors' names. Neither method is really commendable. A classification by subject, even in a special bibliography, would be the proper method, but the work of making such a list is laborious and costly. In addition to deciding on the arrangement, a precise method of quoting each reference should be used. In quoting from a periodical that has both volume and year, both should be given, as one datum serves as check upon possible error in the other. The



bibliography in the book in hand offends a great deal in this respect, the volume being rarely quoted. In many cases a supplementary reference to C. A. is given, with both volume and year. A commendable feature is the use of Arabic numerals for the volume number. The practise of employing Roman numerals for volume numbers is a relic of the middle ages that may well be eliminated in science. The higher numbers are difficult to read and typographic errors are far more likely to occur than with the common figures. An instance of the viciousness of the Roman numeral system came recently to the notice of the writer of this review. A reference was given to *Gilb. Ann.*, iv. It happened that from another source the reference was known to be "lv." It can be seen what a wild goose chase the searcher would have undertaken if the first reference had been the only one at hand. The addition of the year would, of course, have sooner or later put him on the right track, hence the advisability of giving both data. In many cases journals of long standing have been issued in series, and with all such the series should of course be given. It is evident, however, that in the case just mentioned, while iv and lv may be easily confused 4 and 55 can not be.

Turning to the contents of the book in hand, it is found that the subject is presented in much detail and very thoroughly. As the processes discussed are all mechanical at base, many illustrations of apparatus are given. The large number of quotations from patent-literature given in the bibliography will be of great aid to those in charge of recovery plants, who may have developed improvements on existing apparatus and desire to protect their inventions. Brief statements of the important points in many patents are appended to the reference. The author remarks that he has been much surprised to find that many devices that he believed to be new have been long anticipated. His experience in this direction is a common one. Scarcely any process of recent development is without anticipation in some degree. His experiences lead him to the view that so far as regards the basic processes of recovery there is very little opportunity for inventors, but this may be a rash prediction. The "patient search and vigil long" of the inventor is often unexpectedly rewarded. The physical chemistry of the procedures is taken up, and many tables and graphs are given to illustrate and explain the principles involved. The work constitutes a very valuable addition to the literature of chemical engineering, which has developed so extensively of late years in this country, a development that is steadily tending to render the nation independent of others. The mechanical construction of the book is of the excellent type which characterize the productions of the well-known publishing house. The literary style is not of the best. In the general text, which is largely descriptive and formally scientific, this does appear, but the preface is written in a weak style, with an over-use of words. Laxity of literary form seems to be the tendency in American scientific literature. The education of the student in science courses is directed so strongly to the practical side that training in the proper use of words and even in the proper method of speaking is being neglected. Probably the discontinuance of classical study has had something to do with this falling off. However, the merits of this book are in the material presented, and this criticism is merely a personal reaction of the reviewer to some of the setting.

HENRY LEFFMANN.



## PUBLICATIONS RECEIVED.

*The Analysis of Rubber*, by John B. Tuttle, American Chemical Society Monograph Series. 155 pages, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price \$2.50.

*Catalysis in Organic Chemistry*, by Paul Sabatier. Translated by E. Emmet Reid. 406 pages, 8vo. New York, D. Van Nostrand Company, 1922. Price \$5.00.

*Les Applications Élémentaires des Fonctions Hyperboliques a la Science de l'Ingénieur Electricien*, par A. E. Kennelly, Professeur d'électricité appliquée, Université de Harvard. 153 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 15 Francs.

*A First Book in Chemistry*, by Robert H. Bradbury, A.M., Ph.D., Head of the Department of Science, South Philadelphia High School. 687 pages, illustrations, 8vo. New York, John Wiley and Sons, Inc., 1922. Price \$5.00.

*Introduction a la Théorie de la Relativité Calcul Différentiel Absolu et Géométrie*, par H. Galbrun, Docteur es Sciences. 457 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price 60 Francs.

*La Composition de Mathématiques dans l'examen d'admission a l'École Polytechnique de 1901 a 1921*, par F. Michel, M. Potron. Exercices d'application du cours de mathématiques spéciales. 452 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 40 Francs.

*Théorie des Nombres*, par M. Kraitchik avec une préface de M. d'Ocagne. 229 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 25 Francs.

*The Recovery of Volatile Solvents*, by Clark Shove Robinson. First edition. 188 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price \$2.50.

*Belt Conveyors and Belt Elevators*, by Frederic V. Hetzel, M.E. 333 pages, illustrations, 12mo. New York, D. Appleton and Company, 1922.

*Le Tunnel du Simplon*. Sa construction, son achèvement, 1898-1921. En commémoration de la pose de la dernière clef de voûte 4 Decembre, 1921. 47 pages, illustrations, plates, 8vo.

*The Sanitation of Bath Houses*, by Wm. Paul Gerhard, C.E. Reprinted from "Architecture and Building." 16 pages, illustrations, quarto. New York, Author, 1922. Price 60 cents.

*National Advisory Committee for Aeronautics: Technical Notes No. 117, The Synchronization of N.A.C.A. Flight Records*, by W. G. Brown. 3 pages, illustrations, photograph, quarto. No. 118, F-5-L Boat Seaplane-Performance Characteristics, by Lieutenant W. S. Diehl. 8 pages, illustrations, quarto. No. 119, The Elimination of Dead Centre in the Control of Airplanes with Thick Sections, by Thomas Carroll. 3 pages, illustrations, quarto. No. 120, A Preliminary Study of Airplane Performance, by F. H. Norton and W. G. Brown. 7 pages, illustrations, photograph, quarto. Eighth Annual Report, 1922. Administrative report without technical reports. 52 pages, quarto. Washington, Government Printing Office, 1922.



## CURRENT TOPICS.

---

**The Protection of Brass Weights.** J. J. MANLES. (*Phil. Mag.*, Nov., 1922.)—Regular use in the laboratory for sixteen years and numerous re-standardizations have shown that Faraday's method of protecting iron weights is applicable also to weights of brass. The polished weights were heated in a semi-luminous gas flame until they were almost red hot and then were plunged at once into boiled linseed oil, where they remained to cool. After removal they were washed in turpentine and rubbed with old linen. The surface thus acquired a uniform tint of bronze. Recently the repetition of this treatment led to unsatisfactory results, attributed to a change in the chemical composition of the gas used for heating the weights. The following plan was adopted with success. The weight, evenly covered with linseed, was supported upon a few sharp points within a crucible which was then heated in a Bunsen flame. When the weight assumed a golden color the process was complete. After it had cooled in the crucible, the weight was rubbed with an old silk handkerchief and subsequently adjusted. The mass of the layer covering the surface was calculated to be about .00005 grm. per sq. cm.

G. F. S.

**Early Chemical Industry in America** is described by C. A. BROWNE (*Jour. Ind. Eng. Chem.*, 1922, xiv, 1066-1071). The Indians imparted to the first settlers a knowledge of rubber, maple sugar, chocolate, vanilla, cochineal, tapioca starch, and other commodities. The Spanish settlers devised the cold amalgamation or patio process for the extraction of silver from its ores; they and the French smelted the lead ores of Missouri in a crude fashion. The English introduced chemical manufactures. In 1642 the General Court of Massachusetts took measures to insure the manufacture of saltpetre. This compound was manufactured during the War of 1812 from wood ashes and the calcium nitrate deposits of the Mammoth cave.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

---

Vol. 195

FEBRUARY, 1923

No. 2

---

## RECENT AERONAUTIC INVESTIGATIONS AND THE AIRPLANE INDUSTRY.\*

BY

JOSEPH S. AMES, Ph.D., LL.D.

Professor of Physics, The Johns Hopkins University, Baltimore, Maryland; Director, Office of  
Aeronautical Intelligence, National Advisory Committee for Aeronautics.  
Member of the Institute, Associate Editor.

EVERY industry concerned with manufacture relies upon the work of the scientist for the knowledge which makes its existence possible. Progress in the industry may come from increased efficiency in method, from improvements based upon existing knowledge or from new knowledge furnished by scientific laboratories. This last fact is obvious. It is even realized by those who control the industries. Many of our largest manufacturing companies support research laboratories where work of the truest scientific character is carried on, in which the investigators are forbidden to consider the possible practical applications of the fruit of their labor. These enlightened companies know that what is most needed and what is the most difficult to obtain is a continuous increase of knowledge of new facts, new phenomena concerning electricity, radiation, chemical reactions, and, in reality, all nature. The men who can do this research work are not easily found, while those who can apply the new knowledge to practical purposes abound. It happens but rarely that a man has

---

\* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute, held Thursday, November 23, 1922.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.

VOL. 195, NO. 1166—11

145



the ability and patience required to devise and carry on scientific investigations and at the same time can elaborate the processes to make his discoveries useful. A man cannot serve two masters. The worker in pure science, as it has been called, gets his reward from having added to the store of truth vouchsafed to man; and, if his mind runs at times along more practical lines, he may rest assured that there is no scientific discovery, however remote, seemingly, from the processes of daily life, which may not ultimately be made use of in some commercial industry.

An industry which is essentially modern and which is growing in importance daily is that associated with aviation. During the war we saw it grow to manhood from the condition of a baby in an incubator. But the full-grown man was like an athlete developed for a specific purpose. Airplanes for all kinds of military operations were perfected, to such a degree that to most of us to-day an airplane means but one thing, a weapon for war. It is true that those of us who are interested in sports look upon one also as a racing machine, and the fact that danger is associated with the sport makes it for many people all the more interesting. Now, as long as people consider aviation only from the standpoint of warfare or sport, the country as a whole is not interested. This is a fact which should be realized by all who see in aviation greater possibilities. It does obviously offer a method of transportation which when developed will revolutionize our lives as much as the automobile has done in our generation or the steam railroads and steam vessels did in that of our fathers and grandfathers. Before this day can come, however, each of us must be made to realize what aviation will mean to him personally, each day of his life. An airplane as a war machine or as a sporting toy does not concern us, and we will not think seriously about the subject.

As a commercial enterprise, aviation is, however, increasing in importance; and it is one of those industries whose reliance upon scientific investigations is direct and complete. In the years before the war airplanes had been made and flown in sporting events, and it is interesting for an American to recall that the whole science and art are based upon the work of three of our countrymen: Langley and the Wright brothers. Few of us in this country, though, had a vision of the possibilities of aviation; but in Europe it was different. England had a group of men



developing its theoretical features and also performing well-planned experiments in a laboratory maintained by the Government. In France the great engineer Eiffel was carrying on a beautiful series of experiments in a fine laboratory of his own. In Germany Prandtl and others were also at work. So when, at the very outset of the war, the possibilities of aviation became apparent, and as the days went on, its predominating importance was recognized, the European countries had at their disposal a considerable amount of scientific information which could be put to practical use immediately. This was done and this is the explanation of the seemingly magical expansion of aviation.

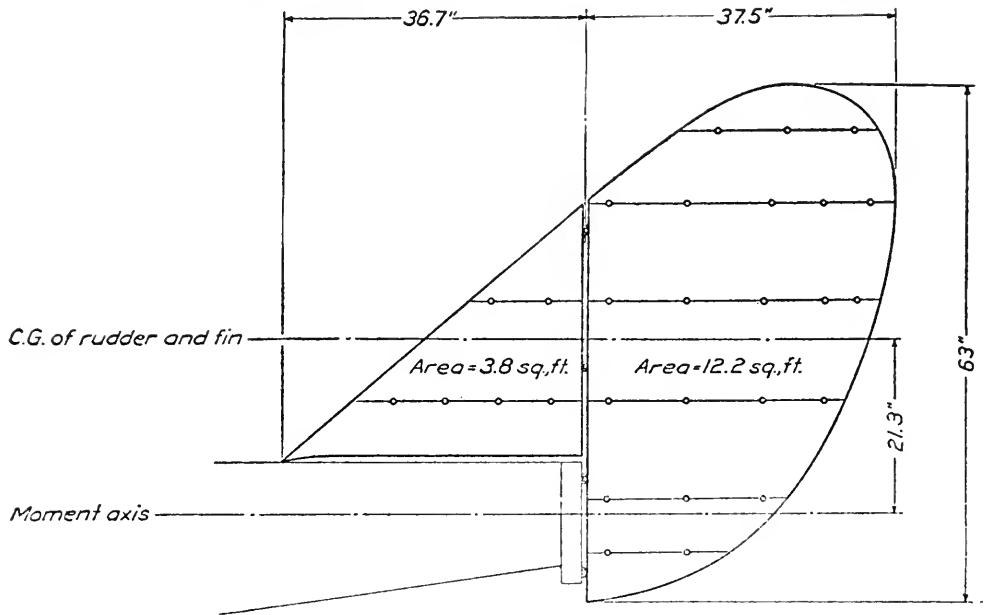
One effect of the war was to make all countries, even our own, realize the need of the intensive study of the scientific facts underlying aeronautics. The only limitation upon this has been the earnest desire of certain governments to economize, for all laboratory investigations are expensive. In this country the government maintains an aerodynamic laboratory at Langley Field, Virginia, under the direct supervision and control of the National Advisory Committee for Aeronautics. The work done here is of a purely scientific nature but, as has been said, no new facts of this kind are learned without being applied sooner or later to a practical purpose. In what follows will be given a few illustrations of this statement:

#### I. DISTRIBUTION OF AIR FORCES OVER AN AIRPLANE.

As every one knows, an airplane is heavier than air and is sustained in flight owing to the dynamical action of the air flowing past its wings, there being produced an increased pressure below the wings and a decreased pressure above. The upward force due to these pressure differences is called the "lift," and it is of interest to note that the greater part of the lift is due to the diminished pressure on the upper side of the wings, so that one may say an airplane is pulled rather than pushed up. Similarly, due to the rapid flow of air there are forces on all the other parts of the airplane: The fuselage, the rudder, the elevator, the stabilizing surface at the rear and the fins. When the airplane is in steady horizontal flight, these forces have certain values; when the airplane is manœuvring, performing a loop, a roll, a dive, etc., all of them change. Further, if the shape or size of any part is altered, the forces are also changed. It is obvious that before



one can design the structure of an airplane or before any satisfactory theory of the behavior of an airplane can be worked out, it is necessary to know the intensity of these forces. It is not sufficient, however, to know the total force acting on a wing, for instance; one must also know how this force is distributed: Is the greater part experienced near one edge or the other? Are there any special areas where the force is greater than at others? Further, how is this distribution affected, by making the airplane manoeuvre or by changing the shapes of its various parts? In order to answer these questions, a long series of experiments

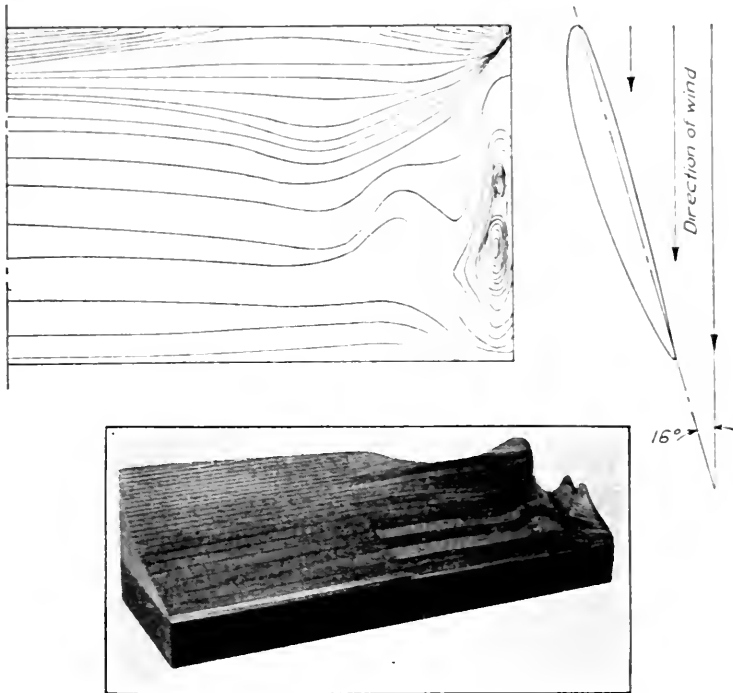


Elevation of fin and rudder showing location of holes.

has been carried out both upon models of airplanes held suspended in a wind-tunnel and upon airplanes in actual flight. The same method is used in both sets of experiments. A series of small holes is made in the surface of the part to be investigated; each of these is connected by a rubber tube to a central instrument, which really is a number of separate instruments, each of which measures the pressure of the air in one tube; the indications of these instruments are photographed simultaneously. By this method the pressures existing at any instant at twenty-five or thirty points of the wing, or whatever part is in question, may be determined. By connecting the apparatus to various parts of an airplane, the distribution of the force, under any specific cir-



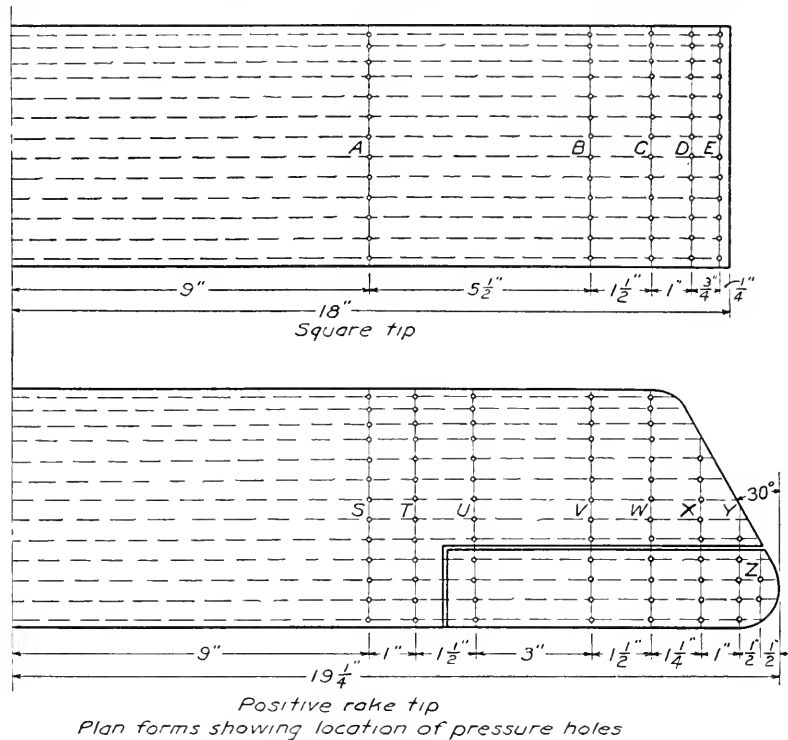
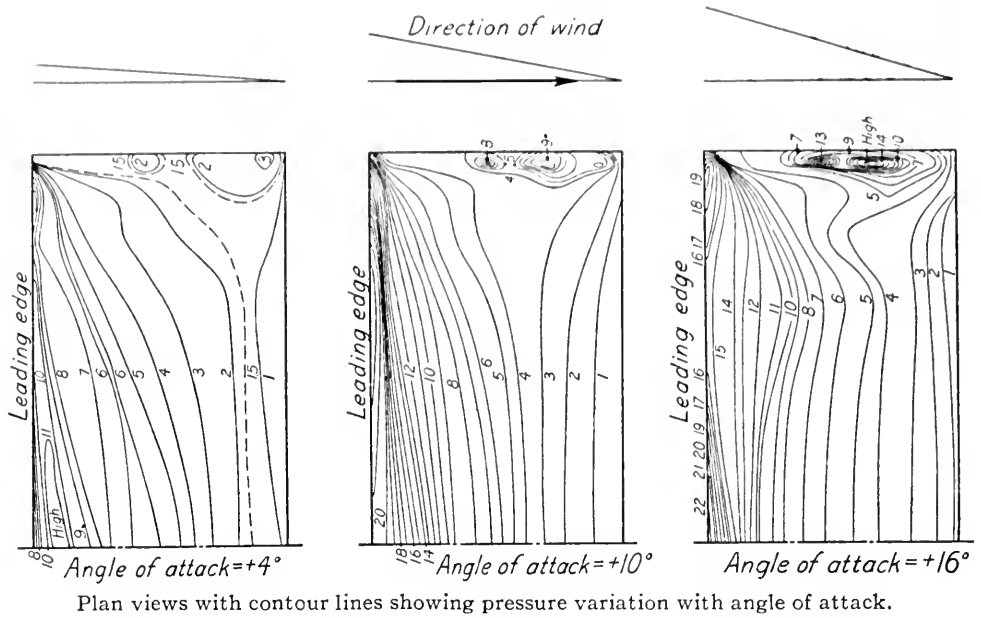
cumstances, may thus be learned. The essential part of the whole device is, of course, the instrument which measures the pressure. Two types are used: One, in case the experiment is upon a model in a wind-tunnel; the other, in case of an airplane in flight. Both instruments are special types of what are called "manometers" in technical laboratories. The former is simply a series of glass tubes, each tube has a basin at its lower end, and the latter end and part of the tube is filled with a liquid, *e.g.*, colored alcohol; if the pressure at the lower end of any tube is increased,



Contour model of loads on square tip wing at 16° angle of attack. Neutral aileron.

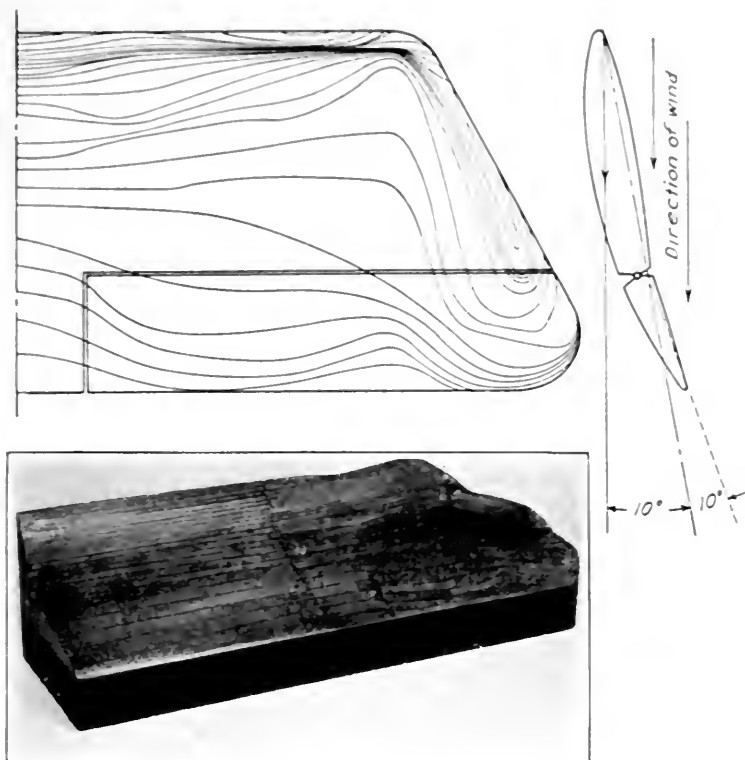
the liquid will rise higher in the tube; if the pressure is lowered, the level of the liquid will fall. Such an instrument could not well be used in an airplane in flight or when making a loop or a roll; so a different type was perfected. This consists essentially of a thin metal diaphragm, held stretched in a metal frame in a closed case, to one side of which is connected the rubber tube leading to the opening in the wing. If the air pressure in this tube increases, the diaphragm will bulge out on the opposite side, while if the pressure decreases, it will bulge in. All that is necessary is to record these slight bending motions of the diaphragm. This is done by attaching to it a small mirror from which a beam of



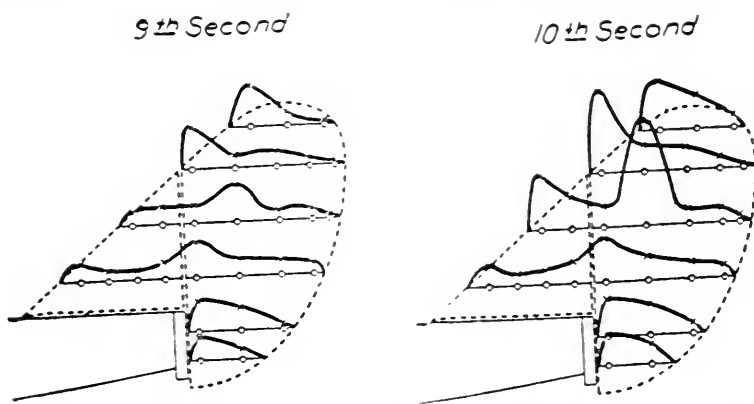


light is reflected onto a photographic film; when the diaphragm is bulged out or in, the mirror is of course rotated in one direction or the other, and so the beam of light is deflected one way or the other. Before any such manometer may be used for measurements it must, of course, be standardized by subjecting it to known pressures and measuring their effect. If the central recording





Contour of loads on wing, with positive rake at  $10^\circ$  angle of attack. Aileron  $10^\circ$  down.



Showing the curves of pressures over the entire surface of the rudder and fin for various intervals of time during a left turn.

instrument has several such manometers it is convenient to adjust them so that they are equally sensitive. This facilitates the interpretation of the photographic records. Little more need be said in regard to the method used in this investigation. The results obtained are most interesting. In a field of study as extensive as this, I am compelled to make a selection; and the cases I shall discuss are as follows:



- (1) The case of an ordinary wing, showing the "peak" of pressure near one corner.
- (2) The effect of the change of angle of attack.
- (3) The effect of changing the plan form of the wing.
- (4) The influence of the aileron.
- (5) The rudder.

All these cases can be described best by models or by topographic drawings. Each model corresponds to a relief map of a country, the elevation at each point being a measure of the pressure at that point, this being the total pressure upward, due to the combined action at the upper and lower surfaces. The principal features are evident from the figures and do not call for explicit description.

Many of the facts brought out in this investigation were entirely unexpected, and all the results are of great importance to one interested in the science of aerodynamics. But to the designer of an airplane the whole series of investigations is of fundamental importance. He can learn first of all what type of wing to adopt, and then what relative strength to give different parts of the structure so as to meet the stresses they will be called upon to stand. In this way he can so plan his machine that it will not be unduly strong at points which do not demand great strength, and thus save cost in material and construction. Further, if it is desired to subject an airplane to loading tests in order to learn accurately its breaking strength, this can now be done intelligently. In the past the custom in making this test has been to turn a wing upside down and put on top bags of sand, increasing the weight of these until the wing broke. No definite way of distributing the sand in order to correspond to actual flying conditions was known, but now it is; and in the future these tests will have a thoroughly practical meaning.

## II. THE MOTION OF AN AIRPLANE IN MANŒUVRES.

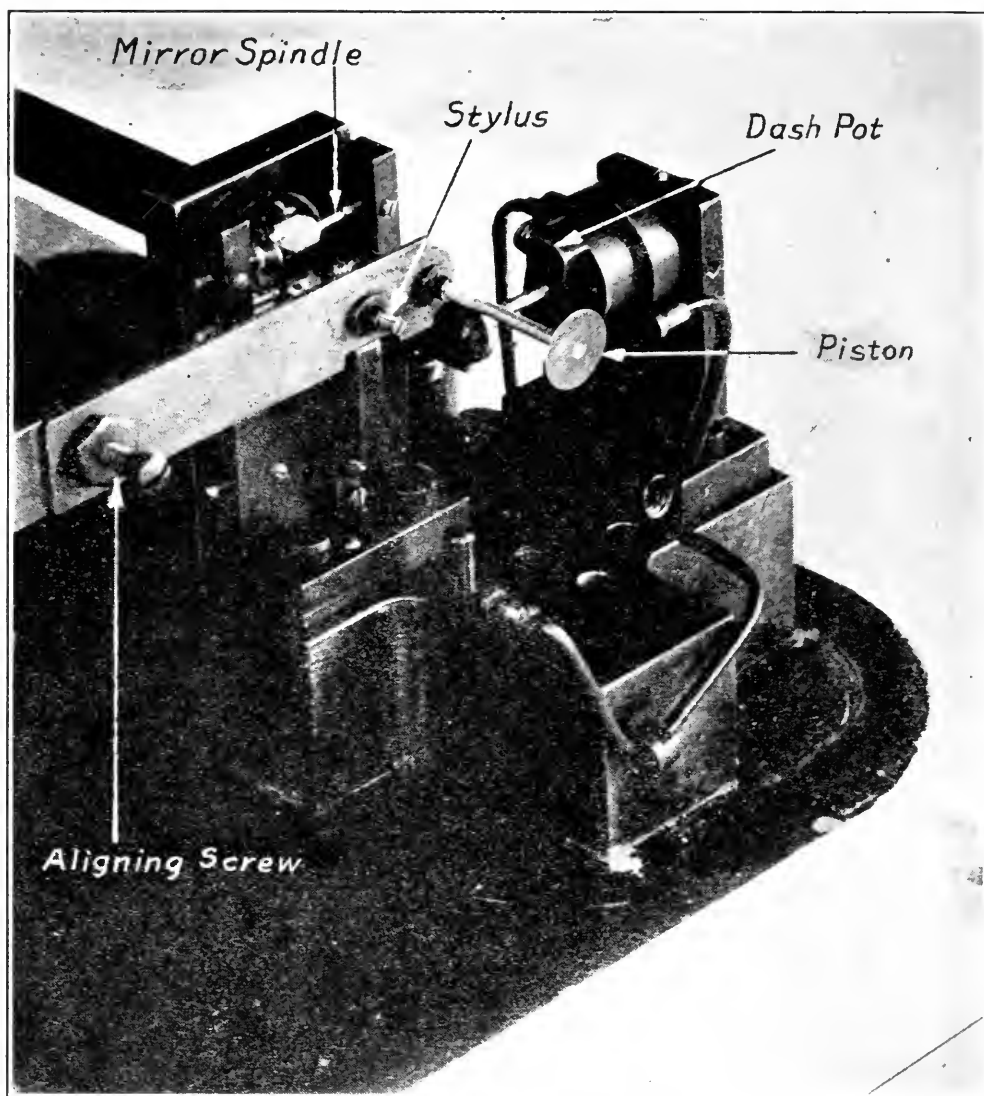
Another investigation had its origin in the need of the theoretical student of aerodynamics to know the exact motion of an airplane at any instant and the effect on this motion of slight changes in the control surfaces, the rudder, the elevator and the ailerons. In order to describe the motion one must know the motion of the centre of gravity—its velocity and acceleration, and also the angular motions about the three axes, *i.e.*, the angular



velocities and the angular accelerations. Instruments for measuring the velocity of an airplane have been in use for many years. The best types make use of the principle that when air is flowing (or when an object is moving through the air) the pressure felt by a body which stops the air is different from that felt in air at rest, and that this impact pressure, as it is called, varies with the velocity of the air. (Anyone who has felt wind blowing against his face or hand is familiar with this fact.) So the air-speed indicator, as it is called, is an instrument for measuring the difference between the impact pressure and the static pressure of the air; from its readings, recorded photographically, the velocity of the airplane may be calculated. Instruments for the measurement of all the other quantities had to be designed and constructed. The matter is complicated because there are three independent directions in which the centre of gravity of the airplane may move; along the line of the shaft of the propeller, sidewise and up; similarly the machine may rotate about any one (or all) of these lines. Therefore any one instrument must in reality be a combination of three instruments. To measure the acceleration in any one direction use is made of a stiff strip of steel, one of whose ends is rigidly held and whose other end will therefore move as the strip bends under the application of the force due to acceleration; the motion of this free end can be recorded photographically; and after the instrument is calibrated or standardized, a measure is obtained of the acceleration in this particular direction. Three of these instruments, combined so as to measure accelerations along three mutually perpendicular directions, form the necessary accelerometer. If the angular velocity around any axis of the airplane is recorded for any length of time, there being made coincidently accurate records of the time, a curve may be drawn expressing the angular velocity as a function of the time. By measuring from the curve the changes in the former per unit of time, values of the angular acceleration are obtained; and also by integrating the curve, as the process is called, that is by working backwards, one can learn through what angle the airplane has turned at any instant. The essential requirements for the instrument are, then, a recording clock and a device to register angular velocity. For a clock a constant speed electric motor serves, and by means of obvious mechanism a sharp line is photographed every second or every two seconds on a rotating



film, superposed upon which are the other records. To measure the angular velocity use is made of a rapidly spinning electric motor mounted as a gyroscope; for, as is well known, if the supports of such a top are rotated around an axis, as would happen in an airplane making manœuvres, the axis of the top itself tends

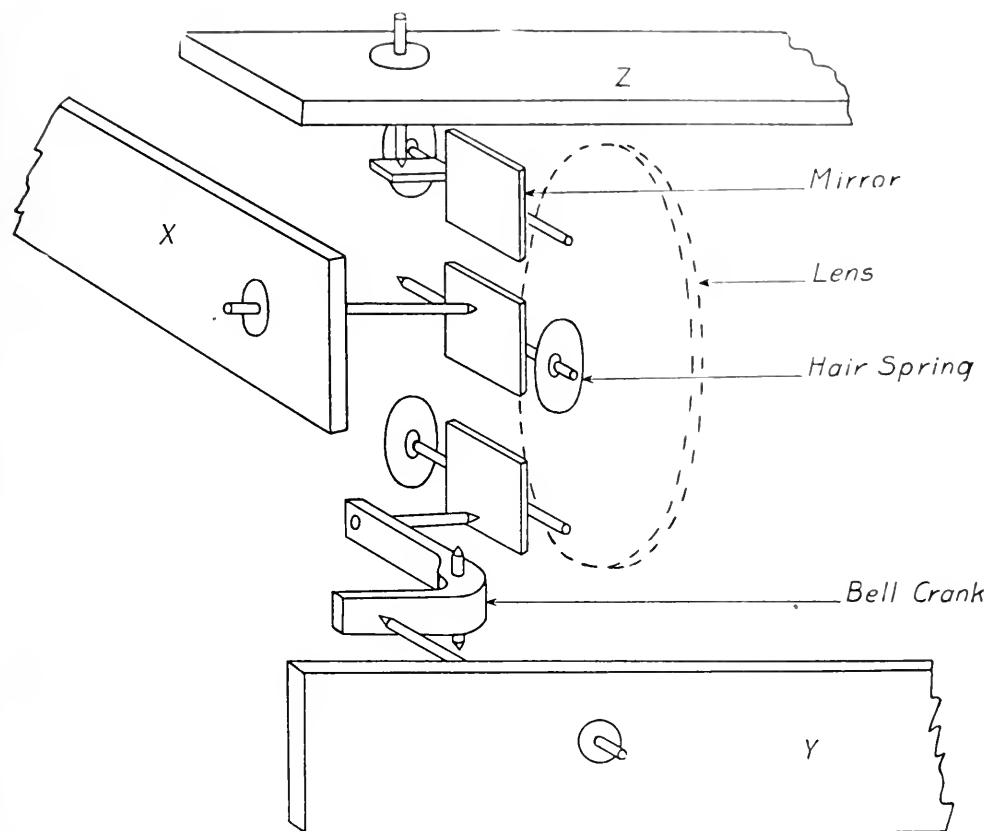


Three component accelerometer.

to move, this motion can be prevented by applying a suitable force, *e.g.*, by a spring, and the intensity of this force—which depends upon the rate of rotation of the airplane—can be measured by photographing the displacement of the spring. Three such gyroscopes, mounted so as to spin about axes mutually perpendicular, will thus serve to record all of the angular velocities of the air-



plane, thus forming an angular velocity meter. To complete the instrumental equipment all that is needed is an instrument to record the motions of the controls. This is extremely simple. A wire leads from each control to a small metal spool which can turn on a metal rod, the connection between the two being by screw threads cut on the outer surface of the rod and the inner surface of the spool—just like a bolt and its nut, a tension spring being introduced. The wire from the control is wound around

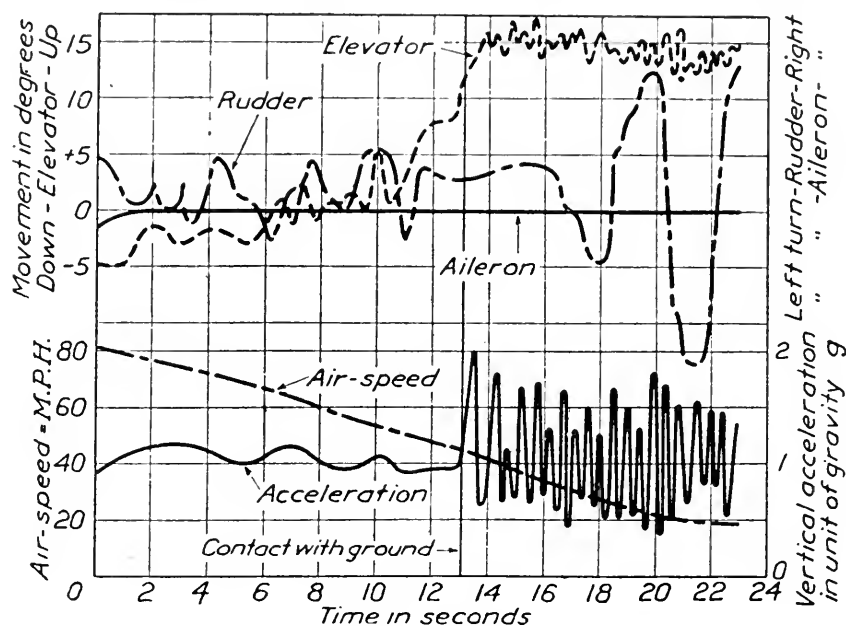


Three component accelerometer, showing the means for transferring the motion of the springs to the three mirrors. The dash pots are omitted.

the spool and fastened to it; so, if the wire is lengthened or shortened, the spool will turn and at the same time slide along its axial rod, in one direction or the other. This sliding motion can be recorded on a photographic film. There are three of these control motions to be recorded, *viz.*, of the rudder, of the elevator, and of the ailerons; and to distinguish between the three records different types of shutters are introduced in the paths of the rays of light coming from the different sliding spools: One makes a dashed photographic record, one a dot and a dash record, and the



third a continuous one. This, with the necessary storage batteries, completes the apparatus needed for the investigation. The airplane under study is equipped with the instruments, which in reality are very compact and light; and, when a manœuvre begins, as for instance a loop, the pilot simply pushes a button, the electric chronometer begins to operate, the gyroscopes begin to spin, the lights required for making the photographic records flash up, and all is ready. After this, everything is automatic. When the pilot lands his machine, the film is developed and the records are



Three-point landing.

measured and studied. There are, of course, numerous records on any one film after any one manœuvre: The straight lines spaced to give time intervals, the three control records, those giving the three components of the acceleration of the centre of gravity, and finally those giving the three components of the angular velocity—10 records in all. Of course for many simple manœuvres a record is taken of only one component of either the acceleration or the angular velocity; so in general the film records do not look complicated. For nearly all purposes it is found useful to calculate from the curve for angular velocity the curves for angular displacement and angular acceleration and to plot these, together with the curve giving the speed of the airplane, on the same photograph; so that one record gives the entire



history of the manœuvre. I shall show a few records of this kind. There is no need of any detailed description, for each tells its own story completely.

- a. Three-point landing.
- b. Taking-off. Tail high.
- c. Taking-off. Tail low.
- d. A loop.
- e. A barrel-roll.
- f. A longitudinal oscillation.

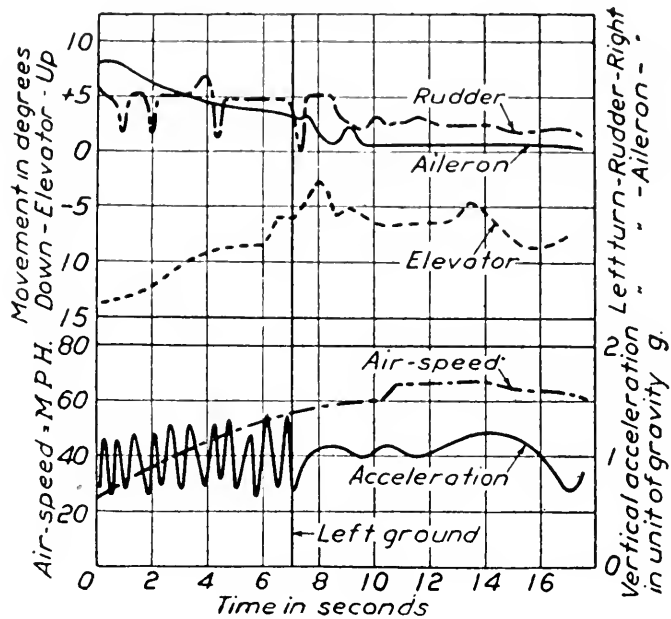
It is obvious that the information to be obtained from records such as these is of the utmost importance to any student of aerodynamics. Here he has practically all the facts concerning the motion of an airplane under the most varied conditions. In order to know the forces which the pilot exerts on the control stick and rudder bar when making manœuvres, there is attached to these a force-recorder, consisting of a carbon pile whose electric resistance changes with pressure. Its readings are recorded on the same photographic film.

Again there are many purely practical questions which can be answered easily from the knowledge available from these records. Is the machine easily controlled? That is, is the work done by the pilot in moving the controls, in order to produce small changes in attitude of the machine, small or great? The answer may be found instantly. Or, is the machine easily manœuvred? That is, can the pilot change the attitude of the machine rapidly? That again can be answered. Or, is the stability great or small? That is, if the machine is disturbed from a condition of steady flight, as, for instance, by an ascending gust of air, will it return to its steady state quickly or not; or, if the disturbance is too great, will it require a change of the controls to make it return at all? All questions of this kind may be investigated with ease. It is seen that we have here an exact scientific method of learning all that we wish to about the performance of an airplane, nothing is left to the memory or to the impressions of a pilot, it is all a matter of record.

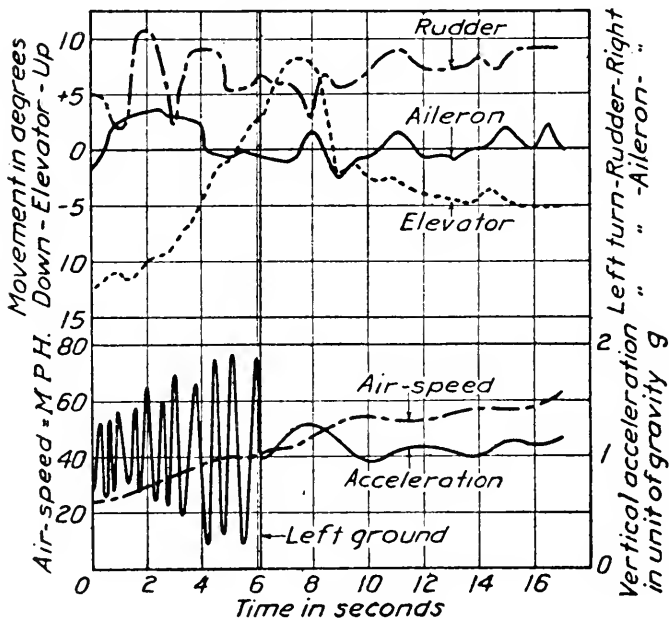
This fact is of the utmost importance in making tests of a new airplane, or of an airplane of a new type. The method in use at present in this country, and in all countries, for carrying out what are called "acceptance tests" of a new airplane, is to send it up in charge of a specially competent pilot, called a "test pilot."



He takes the machine off the ground, flies it steadily, puts it through certain manœuvres, throws it into oscillation, and finally



Tail-high "take-off."

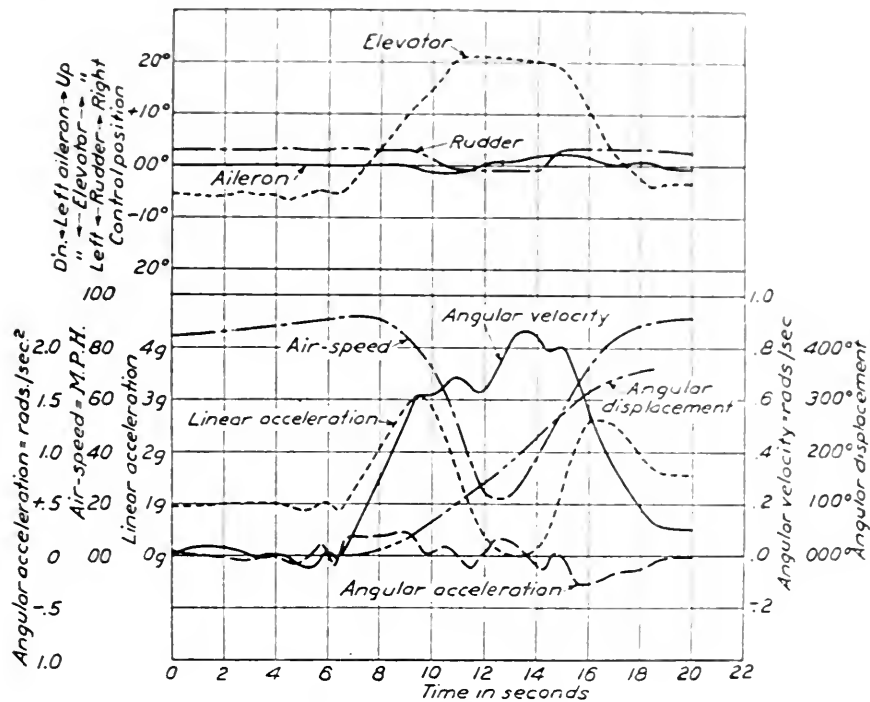


Tail-low "take-off."

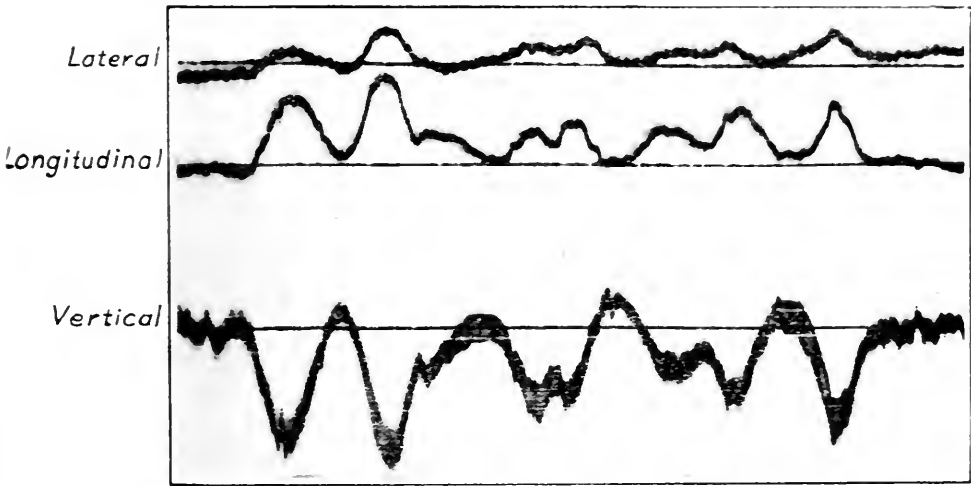
lands it. He then makes a report as to his impressions. Upon what he says rests the decision whether the airplane is accepted or rejected. This may be called a practical method, but it is



certainly not scientific. To begin with, every pilot has a preference for some airplane or for the performance of certain airplanes. These he knows and likes. In testing any new machine,



Loop. Angular velocity about Y-axis.



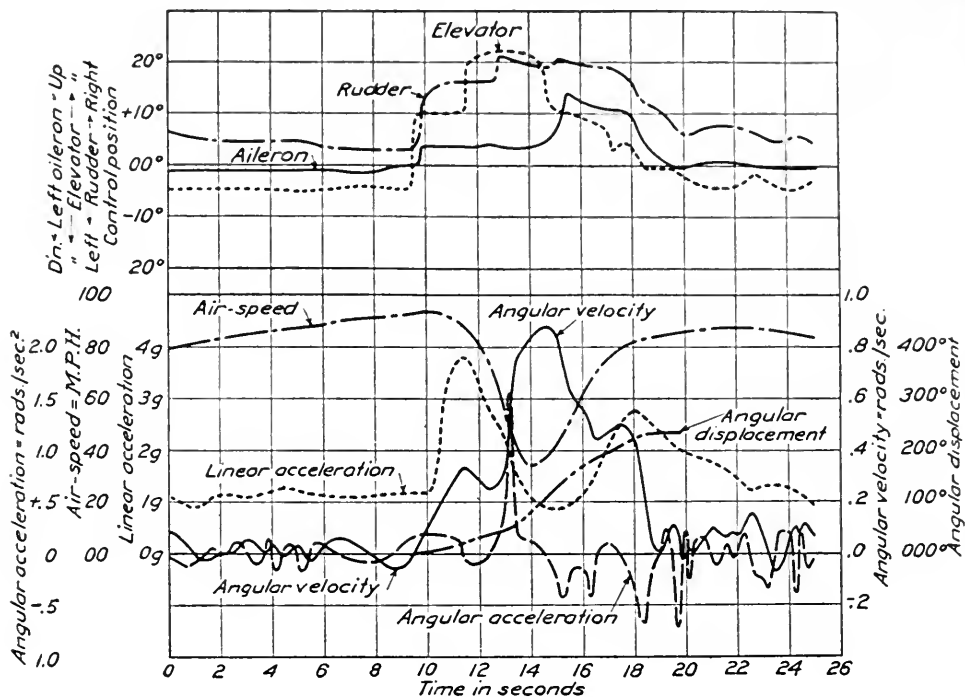
Loop. Two Wing Overs

Three component accelerometer records.

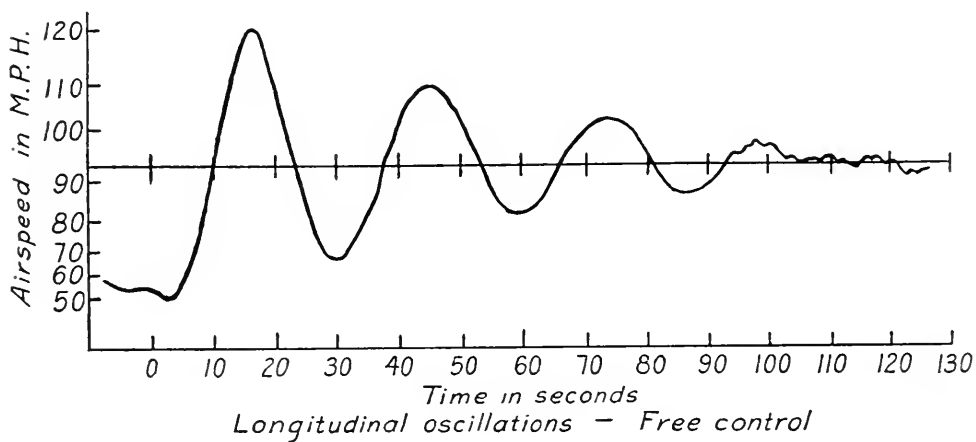
he is of necessity comparing it with another to which he is accustomed. The comparison is never altogether fair. Again, all he has to report are impressions, not necessarily facts; and no man



has sufficiently quick perceptions to note all that happens in such a complicated phenomenon as an airplane manœuvre, nor has he a memory sufficiently accurate to recall all that he did observe.



Barrel-roll to right. Angular velocity about X-axis.



Longitudinal oscillations - Free control

The whole method is bad. But up to the present, it has been the best possible. Now, all this is changed. In place of psychological impressions of certain incidents recorded by an imperfect memory by a man who must be prejudiced to a certain degree, we are able to obtain exact photographic records of what occurs at each instant.



Another obvious application of the method is to the training of pilots. As has been said before, an airplane manoeuvre takes place so quickly that no pilot knows exactly what he does. If he is skilled and therefore has a good "air sense," he does many things by instinct. If he is asked, when he lands, how he did a certain thing, he cannot always tell, and he can never be definite. He can never tell another pilot exactly what he did. He may know in a general way how it was done, but the second pilot has to go up and learn for himself. All this indefiniteness is now obviated; a pilot can get an exact record of what he did to each control in performing any manoeuvre; and this record may be used in instructing a new pilot. Further, pilots will differ in the way in which they effect a loop, a roll or even a landing, and the best of them may learn considerably by comparing his own records with those of other pilots.

### III. THE COMPRESSED AIR WIND-TUNNEL.

Aerodynamics is the science which is concerned with the properties of the air in motion, and of solid bodies in motion with reference to the air. The way in which most of our experimental knowledge of the subject has been obtained has been by supporting solid bodies from balances in a large tube through which air is drawn by means of a suction fan. Such an apparatus is called a wind-tunnel. The balances record the forces and moments required to hold the solid body stationary in spite of the action of the rapidly flowing air-stream. Tunnels have been made as large as 10 or 12 feet in diameter, and fans are used capable of producing velocities from 30 miles an hour to over 200. The size of the solid object immersed in the air-stream is controlled, of course, by the size of the tunnel. By experiments of this character an immense amount of data has been accumulated and many empirical laws have been deduced. (Experiments of the same kind could be conducted on other gases if there were a sufficient supply.) It will be noted that in these experiments there are only two quantities which are varied: The size of the solid object to a limited degree and the velocity of the air. It is evident, however, that the forces acting on the solid body depend upon other things than its size and the velocity of the stream of air. It is clear, for instance, that the force must vary with the density of the air. The force we ourselves



experience if we stop a solid ball is much more intense than it is when we catch a hollow ball of the same size. An increase in the density of the air is an increase in its mass, in its inertia; and this would be felt by the solid body in the tunnel. Again, when a solid is immersed in air, a layer of the air sticks tightly to it, so that as the air-stream flows past the body there is friction, not between the surface of the solid and the moving air, but between the latter and the layer of air adhering to the solid body. This force of friction varies then with the viscosity of the gas, the more viscous it is, the greater is the friction. Therefore, to add to our aerodynamical knowledge we should experiment with an apparatus which allows us to vary the density of the gas and also its viscosity. In order to accomplish the first part of this, namely, to vary the density of the gas, the National Advisory Committee for Aeronautics has had constructed a huge steel tank, inside of which is placed a complete wind-tunnel and in which the air can be kept in a state of compression anywhere between one and twenty atmospheres. The viscosity of the air will be changed slightly by this compression, but not sufficiently to enable one to experiment directly upon its influence. With an apparatus of this kind, the only one so far made in the world, a new source of valuable information is available. It will take several years, however, to systematize it and to make full use of it.

The purpose of this compressed air wind-tunnel is not, however, simply that just given. It has been the custom for many years for designers of aircraft to make models of them of a suitable size to be supported in a wind-tunnel and to have them tested under various conditions, in order to learn whether the ideas which they wished to incorporate in their machines really worked out. Further, in all the aerodynamic laboratories of the world there have been systematic experiments on models of different airplane parts, specially wings, so as to furnish information to the designer. It has long been known that the results obtained from such tests were not altogether conclusive or satisfactory. The operation of the actual airplane showed that its performance was not what would have been expected from the preliminary tests. The reason for this is obvious. Why should an airplane flying through the open air have the same properties as a model, one-twentieth the size or smaller, supported in an



air-stream in the same wind-tunnel? Conditions are fundamentally different. The difference is primarily one of size, and so designers have tried to determine what is called the "scale-effect" and make allowance for it. But the difficulty is that the scale-effect is different for different parts and for different conditions. So while the testing of airplane models in wind-tunnels is still the accepted practice, and a very useful one, it is not as satisfactory as it should be. Fortunately the theory of the flow of air past a solid body reveals a way out of the difficulty. It shows that the properties of an actual airplane of 50 feet span, say, while in actual flight, are the same as those of a model of 2 feet span in a wind-tunnel, provided the air in the tunnel is compressed to a pressure of 25 atmospheres. This means that the change in dimensions of the solid body is compensated for by bringing the molecules of the gas closer together, as is done by compression, provided there is no change in the viscosity of the gas. The actual change in this, being small and known, can be taken into account. The new compressed air wind-tunnel therefore offers a means of learning in advance from experiments on models the characteristics of actual airplanes. It is needless to emphasize the practical importance of this possibility.

If opportunity permitted, I could mention a number of other investigations, purely scientific in their conception, which have an intensely practical interest to the industry. These few illustrations will suffice, however, to emphasize the intimate connection between pure science and industrial needs.

---

**The Variation of the Dielectric Constants of Certain Liquids with Temperature.** M. JEZEWSKI. (*Jour. de Phys. et le Radium*, Aug., 1922.)—In a primary circuit having self-induction and capacity electrical oscillations are set up. Loosely coupled to the first circuit is a second in which oscillations are induced, which have their maximum amplitude when a simple relation between the frequency of the primary oscillations and the inductance and capacity of the secondary circuit holds. A variable capacity here makes it possible to tune the secondary circuit to resonance with the first. After this has been accomplished a capacity having for dielectric the liquid under investigation is put in parallel with the variable condenser. This disturbs the resonance by reason of the increased capacity. To restore the former state the variable capacity must be decreased by an amount equal to the capacity of the liquid condenser. Thus is the



dielectric constant obtainable at various temperatures. To determine when the resonance is at its best, a third circuit is coupled to the second. In it is a crystal detector transmitting current to an Einthoven string galvanometer.

Aniline, nitrobenzene, glycerine and water were studied. In all the dielectric constant grew less as the temperature rose, and in all the decrease was very considerable. For aniline the constant at  $25^{\circ}$  C. was 7.418 and at  $174.5^{\circ}$ , 4.194. Nitrobenzene manifested the greatest change,  $18.6^{\circ}$ , 35.67;  $203.9^{\circ}$ , 15.37. Glycerine,  $17^{\circ}$ , 46.6;  $144.5^{\circ}$ , 28.7. Water,  $2.3^{\circ}$ , 90.7;  $99.5^{\circ}$ , 57.4. A formula proposed by Debye connecting density, temperature and dielectric constant is found to fit the facts well, but the values of certain numerical constants that must be supplied in the formula are in "flagrant disagreement" with Debye's theory.

It is surely a misnomer to call the specific inductive capacity a constant, when experiment shows that it is a variable. G. F. S.

**The Effect of the Admixture of Small Quantities of Iron on the Susceptibility of Diamagnetic Elements.** O. E. FRIVOLT. (*Ann. der Phys.*, Bd. 68, page 356.)—Since the susceptibility of iron is some millions of times as great as that of the diamagnetic elements, a very small quantity of the metal might well mask the magnetic properties of the latter. The purest silver obtainable from a firm of jewelers in Christiana was first investigated. For small magnetizing fields its susceptibility was found to be positive, but for fairly large values it became negative. Silver was then deposited electrolytically from a specimen of the metal already measured and the susceptibility of the element in the form of powder was determined. Change in field strength made little difference in the value of this quantity, nor was any change of sign produced. Next the powder was melted together in an electric furnace in an atmosphere of oxygen. This caused no considerable change in the susceptibility. Silver melted in air acted in the same manner. After deposition the susceptibility was in all cases negative. To the pure silver small quantities of iron were then added. When the iron content amounted to .028 per cent., the susceptibility was found to change from positive to negative with increasing field strengths, as was the case with the commercial metal. These experiments emphasize anew the necessity of having pure elements for magnetic investigations. G. F. S.

**Panama Canal Business.**—The *Commerce Monthly*, published by the National Bank of Commerce of New York City, states that the tonnage passing through the Canal during the third quarter of 1922 was 50 per cent. greater than that of the corresponding period of 1921, constituting a new high record. The tonnage increased steadily during 1919 and 1920, but fell off in the following year. During 1922, however, the business has steadily increased and reached amounts which fully set off the former decline. H. L.



## ALTERNATING CURRENT CABLE TELEGRAPHY.\*

BY

LOUIS COHEN, Ph.D.

Consulting Engineer, Signal Corps, U.S.A.

THE use of alternating currents for cable telegraphy was first proposed by General George O. Squier some years ago. In his paper entitled "On an Unbroken Alternating Current for Cable Telegraphy" presented before The Physical Society of London in 1915,<sup>1</sup> he discussed at length the advantages of the alternating current method and described a scheme for the practical operation of the system. He proposed to use an unbroken alternating current continuously acting on the cable and effecting the signalling by varying the amplitudes of successive half cycles or multiples thereof in different degrees for dashes, dots and spaces. General Squier emphasized the advantages of the a. c. method on several occasions, pointing out that a better balance could be obtained on the duplex bridge, sharper definition of signals, and higher speed. Undoubtedly, the alternating current system offers many advantages, certainly in the matter of bridge balance it should prove to be superior to the battery spark system. The disturbances produced by a sudden break in the cable circuit, which is the method of signalling by the battery system, is the worst possible condition for the bridge balance. There are other differences in the two systems, alternating current *versus* direct current, which are of a more or less fundamental character and merit extensive study.

We have a considerable amount of theory and experimental data on the d. c. system of cable telegraphy, a number of investigators have contributed to the study of this problem, Doctor Heaviside's masterly discussion of the many problems connected with d. c. cable telegraphy will remain for a long time the classic work on this subject, he has covered almost every conceivable phase of the subject. For the a. c. system, however, we have very little experimental data, and practically no theory. The only discussion on the subject to my knowledge is the chapter on Sine

---

\* Communicated by General George O. Squier, Chief Signal Officer. U.S.A., and Associate Editor of this JOURNAL.

<sup>1</sup> *Proceedings of the Physical Society of London*, Vol. 27, Part V, August 15, 1915.



Wave Transmission in the excellent book, "Theory of the Submarine Telegraph and Telephone Cable" by H. W. Malcolm. Unfortunately, the mathematical treatment of this section by Malcolm is defective and leads to erroneous conclusions, as will be pointed out further on.

In this paper I shall limit the discussion to a study of the so-called arrival curves for an impressed sinusoidal e.m.f. on a cable with and without terminal apparatus, and compare the results with those given by Doctor Malcolm in his book. It is, of course, very important that we should first of all establish a correct theory of the subject.

In a previous paper, "Electrical Oscillations on Lines,"<sup>2</sup> I have considered the general problem of transient currents on a line, taking into consideration all the electrical constants of the line, *i.e.*, inductance, capacity, resistance and leakage, and have shown that by neglecting the inductance and the leakage, the solution applies to the ocean cable telegraph problem. To facilitate, however, the discussion of this specific problem, I shall give here briefly the derivation of the formulæ used in this paper. Designating by  $R$  and  $C$  the resistance and capacity of the cable and neglecting the inductance, we have the following circuit equations giving the voltage current relation for any element of the cable,

$$\left. \begin{aligned} RI &= -\frac{dV}{dx}, \\ CpV &= -\frac{dI}{dx} \end{aligned} \right\} \quad (1)$$

$p$  is the time differential operator,  $p = \frac{d}{dt}$ .

By substitution from the second equation into the first, we obtain the equation of propagation,

$$\frac{d^2 V}{dx^2} = q^2 V, \quad (2)$$

$$q^2 = RCp. \quad (3)$$

The solution of equation (2) is

$$V = A\varepsilon^{qx} + B\varepsilon^{-qx}. \quad (4)$$

By the aid of either equation of (1) we get the expression for the current at any point on the cable,

$$I = \frac{q}{R} \left\{ -A\varepsilon^{qx} + B\varepsilon^{-qx} \right\}. \quad (5)$$

---

<sup>2</sup> JOURNAL OF THE FRANKLIN INSTITUTE, January, 1923, Vol. 195, No. 1.



The constants  $A$  and  $B$  are to be determined by the terminal conditions. Consider first the simplest case that of a free cable, no terminal apparatus, an e.m.f. impressed at one end of the cable and grounded at the other end. The terminal conditions in this case are,

$$\left. \begin{array}{l} \text{for } x = 0, V = E\epsilon^{j\omega t}, \\ \text{for } x = l, V = 0, \end{array} \right\} \quad (6)$$

assuming a sinusoidal e.m.f. impressed on the cable. Since the complex function  $\epsilon^{j\omega t}$  is used above in place of the Sine function, only the real part is to be used in the final results.

Substituting the values from (6) into (4), we get

$$\left. \begin{array}{l} A + B = E\epsilon^{j\omega t}, \\ A\epsilon^{ql} + B\epsilon^{-ql} = 0. \end{array} \right\} \quad (7)$$

The values of  $A$  and  $B$  are readily determined from the above two equations, as follows:

$$\left. \begin{array}{l} A = \frac{-E\epsilon^{-ql}j\omega t}{\epsilon^{ql} - \epsilon^{-ql}}, \\ B = \frac{E\epsilon^{ql}}{\epsilon^{ql} - \epsilon^{-ql}}\epsilon^{j\omega t}. \end{array} \right\} \quad (8)$$

Substituting these values in (4) and (5), we get the expressions for the voltage and current at any point on the cable,

$$\left. \begin{array}{l} V = \frac{E\{\epsilon^{q(l-x)} - \epsilon^{-q(l-x)}\}}{\epsilon^{ql} - \epsilon^{-ql}}\epsilon^{j\omega t} \\ \quad = \frac{E \operatorname{Sinh} q(l-x)}{\operatorname{Sinh} ql}\epsilon^{j\omega t}, \\ I = \frac{q}{R} E \frac{\operatorname{Cosh} q(l-x)}{\operatorname{Sinh} ql}\epsilon^{j\omega t}. \end{array} \right\} \quad (9)$$

In the above expressions  $q$  includes the time differential operator  $p$  which is so far indeterminate. Utilizing the method I have developed in my paper on "Electrical Oscillations on Lines,"<sup>3</sup> we write,

$$\frac{ql}{\operatorname{Sinh} ql} = 1 - \frac{2}{1 + \left(\frac{\pi}{ql}\right)^2} + \frac{2}{1 + \left(\frac{2\pi}{ql}\right)^2} - \frac{2}{1 + \left(\frac{3\pi}{ql}\right)^2} + \dots \quad (10)$$

Now consider first term of the above series,

$$\frac{1}{1 + \left(\frac{\pi}{ql}\right)^2} = \frac{1}{1 + \frac{\pi^2}{RCi^2p}} = \frac{1}{1 + \frac{m}{t}}, \quad \left(m = \frac{\pi^2}{RCi^2}\right) \quad (11)$$

<sup>3</sup> Loc. cit.



expanding in a series, we have

$$\frac{1}{1 + \frac{m}{p}} = 1 - \frac{m}{p} + \frac{m^2}{p^2} - \frac{m^3}{p^3} + \dots \quad (12)$$

Operating by this series on  $\varepsilon^{\gamma t}$ , replacing  $j\omega$  by  $\gamma$  for simplicity, we get

$$\begin{aligned} \frac{1}{p} \varepsilon^{\gamma t} &= \int_0^t \varepsilon^{\gamma t} dt = \frac{1}{\gamma} \varepsilon^{\gamma t} - \frac{1}{\gamma} \\ \frac{1}{p^2} \varepsilon^{\gamma t} &= \int_0^t \int_0^t \varepsilon^{\gamma t} dt = \frac{1}{\gamma^2} \varepsilon^{\gamma t} - \frac{1}{\gamma^2} - \frac{1}{\gamma} t \\ \frac{1}{p^3} \varepsilon^{\gamma t} &= \frac{1}{\gamma^3} \varepsilon^{\gamma t} - \frac{1}{\gamma^3} - \frac{1}{\gamma^2} t - \frac{1}{\gamma} \frac{t^2}{2} \\ &\dots \dots \dots \\ \frac{1}{p^m} \varepsilon^{\gamma t} &= \frac{1}{\gamma^m} \varepsilon^{\gamma t} - \frac{1}{\gamma^m} - \frac{1}{\gamma^{m-1}} t - \frac{1}{\gamma^{m-2}} \frac{t^2}{2} - \frac{1}{\gamma^{m-3}} \frac{t^3}{3} - \frac{1}{\gamma^{m-4}} \frac{t^4}{4} - \dots \end{aligned} \quad (13)$$

Substituting from (13) in (12) and rearranging, we have

$$\begin{aligned} \frac{1}{1 + \frac{m}{p}} \varepsilon^{\gamma t} &= \varepsilon^{\gamma t} \left( 1 - \frac{m}{\gamma} + \frac{m^2}{\gamma^2} - \frac{m^3}{\gamma^3} + \dots \right) \\ &\quad + \frac{m}{\gamma} \left( 1 - \frac{m}{\gamma} + \frac{m^2}{\gamma^2} - \frac{m^3}{\gamma^3} + \dots \right) \\ &\quad - \frac{m}{\gamma} m t \left( 1 - \frac{m}{\gamma} + \frac{m^2}{\gamma^2} - \frac{m^3}{\gamma^3} + \dots \right) \\ &\quad + \frac{m}{\gamma} \frac{m^2 t^2}{2} \left( 1 - \frac{m}{\gamma} + \frac{m^2}{\gamma^2} - \frac{m^3}{\gamma^3} + \dots \right) \\ &\quad - \dots \dots \dots \\ &= \frac{1}{1 + \frac{m}{\gamma}} \varepsilon^{\gamma t} + \frac{m}{\gamma} \frac{1}{1 + \frac{m}{\gamma}} \left( 1 - m t + \frac{m^2 t^2}{2} - \frac{m^3 t^3}{3} + \dots \right) \\ &= \frac{1}{1 + \frac{m}{\gamma}} \left\{ \varepsilon^{\gamma t} + \frac{m}{\gamma} \varepsilon^{-m t} \right\}. \end{aligned} \quad (14)$$

Operating in the same way on  $\varepsilon^{\gamma t}$  by the other terms of the series (10) and collecting the results, we get

$$\begin{aligned} \frac{ql}{\sinh ql} \varepsilon^{\gamma t} &= \varepsilon^{\gamma t} - \frac{2 \left( \varepsilon^{\gamma t} + \frac{m}{\gamma} \varepsilon^{-m t} \right)}{1 + \frac{m}{\gamma}} + \frac{2 \left( \varepsilon^{\gamma t} + \frac{4m}{\gamma} \varepsilon^{-4m t} \right)}{1 + \frac{4m}{\gamma}} \\ &\quad - \frac{2 \left( \varepsilon^{\gamma t} - \frac{9m}{\gamma} \varepsilon^{-9m t} \right)}{1 + \frac{9m}{\gamma}} + \dots \end{aligned} \quad (15)$$



We may write equation (15) in the following form :

$$\frac{ql}{\text{Sinh } ql} \epsilon^{\gamma t} = \epsilon^{\gamma t} \left\{ 1 - \frac{2}{1 + \frac{m}{\gamma}} + \frac{2}{1 + \frac{4m}{\gamma}} - \frac{2}{1 + \frac{9m}{\gamma}} + \dots \dots \right\} \\ - \frac{2m}{\gamma} \left\{ \frac{\epsilon^{-mt}}{1 + \frac{m}{\gamma}} - \frac{4\epsilon^{-4mt}}{1 + \frac{4m}{\gamma}} + \frac{9\epsilon^{-9mt}}{1 + \frac{9m}{\gamma}} - \dots \dots \right\} \tag{16}$$

By inspection it is seen that the series of the first bracket in (16) is of the same form as the series (10), except that  $\frac{\pi^2}{q^2 l^2}$  is replaced by  $\frac{m}{\gamma}$ , the sum of the series is therefore equal to

$$\frac{\pi \sqrt{\frac{\gamma}{m}}}{\text{Sinh } \pi \sqrt{\frac{\gamma}{m}}}.$$

Hence

$$\frac{ql}{\text{Sinh } ql} \epsilon^{\gamma t} = \frac{\pi \sqrt{\frac{\gamma}{m}}}{\text{Sinh } \pi \sqrt{\frac{\gamma}{m}}} \epsilon^{\gamma t} + \frac{2m}{\gamma} \sum_1^{\infty} \frac{(-1)^n n^2 \epsilon^{-n^2 mt}}{1 + \frac{n^2 m}{\gamma}}. \tag{17}$$

To get the expression for the voltage on the cable the above is to be operated on by  $\frac{E \text{Sinh } q(l-x)}{ql}$ . The series of this factor involves only even powers of  $q$  and therefore integral powers of  $p$ , thus

$$\frac{\text{Sinh } q(l-x)}{ql} = \frac{q(l-x) + \frac{q^3(l-x)^3}{|3|} + \frac{q^5(l-x)^5}{|5|} + \dots}{ql} \\ = \left(1 - \frac{x}{l}\right) + \frac{q^2 l^2 \left(1 - \frac{x}{l}\right)^3}{|3|} + \frac{q^4 l^4 \left(1 - \frac{x}{l}\right)^5}{|5|} + \dots \tag{18}$$

and operating by the above on (17) involves only time differentiation. Operating on the first term of (17), we have

$$q^2 l^2 \epsilon^{\gamma t} = R C l^2 p \epsilon^{\gamma t} = R C l^2 \gamma \epsilon^{\gamma t} = \frac{\pi^2 \gamma}{m} \epsilon^{\gamma t}, \\ q^4 l^4 \epsilon^{\gamma t} = R^2 C^2 l^4 p^2 \epsilon^{\gamma t} = R^2 C^2 l^4 \gamma^2 \epsilon^{\gamma t} = \frac{\pi^4 \gamma^2}{m^2} \epsilon^{\gamma t}, \\ \dots \dots \dots$$

hence

$$\frac{\text{Sinh } q(l-x)}{ql} \epsilon^{\gamma t} = \frac{\text{Sinh } \pi \sqrt{\frac{\gamma}{m}} \left(1 - \frac{x}{l}\right)}{\pi \sqrt{\frac{\gamma}{m}}} \epsilon^{\gamma t}. \tag{19}$$



Similarly operating by (18) on the summation term of (17),

$$\begin{aligned} q^2 l^2 \varepsilon^{-n^2 m t} &= R C l^2 p \varepsilon^{-n^2 m t} = -R C l^2 n^2 m \varepsilon^{-n^2 m t} = -\pi^2 n^2 \varepsilon^{-n^2 m t}, \\ q^4 l^4 \varepsilon^{-n^2 m t} &= R^2 C^2 l^4 p^2 \varepsilon^{-n^2 m t} = R^2 C^2 l^4 n^4 m^2 \varepsilon^{-n^2 m t} = \pi^4 n^4 \varepsilon^{-n^2 m t}, \\ &\dots \dots \dots \end{aligned}$$

For all the terms in the series (18),

$$\begin{aligned} &\frac{\text{Sinh } q(l-x)}{q l} \varepsilon^{-n^2 m t} \\ &= \left\{ \left(1 - \frac{x}{l}\right) - \frac{\pi^2 n^2 \left(1 - \frac{x}{l}\right)^3}{13} + \frac{\pi^4 n^4 \left(1 - \frac{x}{l}\right)^5}{15} - \dots \dots \right\} \varepsilon^{-n^2 m t} \\ &= \left(1 - \frac{x}{l}\right) \left\{ 1 - \frac{n^2 \pi^2}{13} \left(1 - \frac{x}{l}\right)^3 + \frac{n^4 \pi^4}{15} \left(1 - \frac{x}{l}\right)^5 - \dots \dots \right\} \varepsilon^{-n^2 m t} \\ &= \left(1 - \frac{x}{l}\right) \frac{\text{Sin } n\pi \left(1 - \frac{x}{l}\right)}{n\pi \left(1 - \frac{x}{l}\right)} \varepsilon^{-n^2 m t} = \frac{\text{Sin } n\pi \left(1 - \frac{x}{l}\right)}{n\pi} \varepsilon^{-n^2 m t}. \quad (20) \end{aligned}$$

Substituting the values from (19) and (20) in (17), we get the following expression for the voltage on the cable:

$$V = \frac{E \text{Sinh } \pi \sqrt{\frac{\gamma}{m}} \left(1 - \frac{x}{l}\right)}{\text{Sinh } \pi \sqrt{\frac{\gamma}{m}}} \varepsilon^{\gamma t} + 2E \frac{m}{\gamma} \sum_1^{\infty} (-1)^n \frac{n^2 \text{Sin } n\pi \left(1 - \frac{x}{l}\right)}{n\pi \left(1 + \frac{n^2 m}{\gamma}\right)} \varepsilon^{-n^2 m t}. \quad (21)$$

Replacing  $m$  by its equivalent  $\frac{\pi^2}{RC l^2}$  and  $\gamma$  by  $j\omega$  and simplifying, we obtain

$$V = \frac{E \text{Sinh } \sqrt{j\omega RC} (l-x)}{\text{Sinh } \sqrt{j\omega RC} l} \varepsilon^{j\omega t} + 2E \sum_1^{\infty} (-1)^n \frac{n\pi \text{Sin } n\pi \left(1 - \frac{x}{l}\right)}{j\omega RC l^2 + n^2 \pi^2} \varepsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \quad (22)$$

The expression for the current on the cable is readily obtained from (22) by the relation

$$\begin{aligned} I &= -\frac{1}{R} \frac{dV}{dx} \\ I &= \frac{E \sqrt{j\omega RC}}{R} \frac{\text{Cosh } \sqrt{j\omega RC} (l-x)}{\text{Sinh } \sqrt{j\omega RC} l} \varepsilon^{j\omega t} + \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \frac{n^2 \pi^2 \text{Cos } n\pi \left(1 - \frac{x}{l}\right)}{j\omega RC l^2 + n^2 \pi^2} \varepsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \quad (23) \end{aligned}$$

The real parts of above equations (22) and (23) are the complete expressions for the voltage and current distributions on the cable. The first terms of the right-hand side of equations (22) and (23) give the steady state, periodic component of voltage



and current and the other terms the transient voltage and current. We may put for convenience

$$\left. \begin{aligned} V &= V_s + V_t, \\ V_s &= \frac{E \sinh \sqrt{j\omega RC} (l-x)}{\sinh \sqrt{j\omega RC} l} \epsilon^{j\omega t}, \\ V_t &= 2E \sum_1^{\infty} (-1)^n \frac{n\pi \sin n\pi \left(1 - \frac{x}{l}\right)}{j\omega RC l^2 + \pi^2 n^2} \epsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \end{aligned} \right\} \quad (24)$$

$$\left. \begin{aligned} I &= I_s + I_t, \\ I_s &= \frac{E \sqrt{\frac{j\omega C}{R}} \cosh \sqrt{j\omega RC} (l-x)}{\sinh \sqrt{j\omega RC} l} \epsilon^{j\omega t}, \\ I_t &= \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \frac{n^2 \pi^2 \cos n\pi \left(1 - \frac{x}{l}\right)}{j\omega RC l^2 + n^2 \pi^2} \epsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \end{aligned} \right\} \quad (25)$$

For the current at the receiving end of the cable,  $x=l$ , the above reduce to

$$\left. \begin{aligned} I_s &= \frac{E \sqrt{\frac{j\omega C}{R}}}{\sinh \sqrt{j\omega RC} l} \epsilon^{j\omega t}, \\ I_t &= \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \frac{n^2 \pi^2}{j\omega RC l^2 + \pi^2 n^2} \epsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \end{aligned} \right\} \quad (26)$$

The formula for  $I_t$  given by (26) agrees with the one obtained by Malcolm by a different method, and given in his book equation (9), page 363. Malcolm made the error, however, in taking the imaginary part of the equation for calculating the received current instead of the real part as he should have done. This, of course, vitiates all his numerical calculations. In his discussion of "The Influence of Terminal Apparatus," Sine Wave Transmission, he made a more fundamental error in theory as will be shown further on. Taking the real parts of (26), we get for the received current,

$$\left. \begin{aligned} \bar{I}_s &= \frac{E \sqrt{\frac{\omega C}{R}} \cos \left( \omega t - \sqrt{\frac{RC\omega}{2}} l + \frac{\pi}{4} \right)}{\sinh \sqrt{\frac{RC\omega}{2}} l}, \\ I_t &= \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \frac{n^4 \pi^4}{\omega^2 R^2 C^2 l^4 + n^4 \pi^4} \epsilon^{-\frac{n^2 \pi^2}{RC l^2} t}. \end{aligned} \right\} \quad (27)$$



Putting  $\omega = 0$  equations (22) and (23) reduce to

$$\left. \begin{aligned} V &= V_s + V_t = E \left( 1 - \frac{x}{l} \right) + 2E \sum_1^{\infty} \frac{(-1)^n \sin n\pi \left( 1 - \frac{x}{l} \right)}{n\pi} \varepsilon^{-\frac{n^2\pi^2}{RCl^2}t}, \\ I &= I_s + I_t = \frac{E}{Rl} + \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \cos n\pi \left( 1 - \frac{x}{l} \right) \varepsilon^{-\frac{n^2\pi^2}{RCl^2}t}. \end{aligned} \right\} \quad (28)$$

which are the well-known expressions for the voltage and current distribution on a cable for constant e.m.f. For  $x = l$  and  $\omega = 0$  the second equation of (28) reduces to

$$I = \frac{E}{Rl} + \frac{2E}{Rl} \sum_1^{\infty} (-1)^n \varepsilon^{-\frac{n^2\pi^2}{RCl^2}t}. \quad (29)$$

To calculate the transient component of the received current the second equation of (27) is to be used. By taking the imaginary part of (26) Malcolm arrives at the following expression for the transient component of the received current:

$$I = \frac{2E}{Rl} \sum_1^{\infty} \frac{\varepsilon^{-\frac{n^2\pi^2}{RCl^2}t} \cos(m-1)\pi}{\frac{\omega RCl^2}{n^2\pi^2} + \frac{n^2\pi^2}{\omega RCl^2}}. \quad (30)$$

(See Malcolm, page 363, equation 11.)

It is quite obvious that this expression is wrong, putting  $\omega = 0$  leads to the result  $I_t = 0$ .

The difference in the results obtained in any practical case by the use of formula (27), which is the correct formula and Malcolm's formula (30), is very marked. For the purpose of comparison I will use the same cable data that Malcolm used in his calculations. He took the data of the San Francisco-Honolulu section of the Commercial Cable Company,

$$l = 2,276.4 \text{ n. ms.}$$

$$R = 2.1856 \text{ ohms per n. m.}$$

$$C = 0.3842 \text{ mfd. per n. m.}$$

$$Rl = 4975 \text{ ohms.}$$

$$Cl = 874.6 \text{ mfd.}$$

$$RCl^2 = 4.3514 \text{ secs.}$$

Assume a frequency of 10 cycles per second,

$$\omega = 2\pi \times 10 = 62.832, \quad \omega^2 R^2 C^2 l^4 = 74,753.$$

Applying these numerical values to formula (27) and calculating for values of  $n$  from 1 to 6, we get the following tables:



TABLE I.

<i>n</i>	$n^4 \pi^4$	$\frac{n^4 \pi^4}{n^4 \pi^4 + \omega^2 K^2 C^2 l^4}$
1	97.417	0.00132
2	1,558.67	0.0204
3	7,890.78	0.0955
4	24,938.75	0.2501
5	60,985.6	0.4487
6	126,252	0.6281

The values of  $\frac{2}{Rl} \varepsilon^{-\frac{n^2 \pi^2}{K C l^2} t}$  for this particular cable were calculated by Malcolm and given in his book, Table 58, page 302, which is reproduced here, the values given in the table are in microamperes per volt.

TABLE II.

<i>t</i> (secs.)	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.5	2	3
<i>n</i> = 1	320.4	255.4	203.6	162.3	129.3	82.2	41.6	13.4	4.3	0.5
<i>n</i> = 2	162.3	65.5	26.4	10.7	4.3	0.7	0.1	....	...	...
<i>n</i> = 3	52.2	6.8	0.9	0.1	....	....	....	....	...	...
<i>n</i> = 4	10.7	0.3	....	....	....	....	....	....	...	...
<i>n</i> = 5	1.4	....	....	....	....	....	....	....	...	...
<i>n</i> = 6	0.1	....	....	....	....	....	....	....	...	...

Multiplying each of the values of Table II by the values given in the last column of Table I and taking account of the factor  $(-1)^n$  in formula (27) the values given in Table III are calculated from which the received current at different times after the application of the e.m.f. is calculated and given in the last line.

By Malcolm's formula given in his book on page 365, Table 82, the corresponding values are as follows:

<i>t</i> (secs.)	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.5	2	3
<i>I<sub>r</sub></i>	-0.045	+1.814	+3.852	+4.371	+4.055	+2.862	+1.493	+0.483	+0.155	+0.016

The difference in the results obtained by the two formulæ is shown graphically by the curves of Figs. 1 and 2. The periodic component of the received current is the same in both cases, the amplitude is 0.057 microampere per volt.

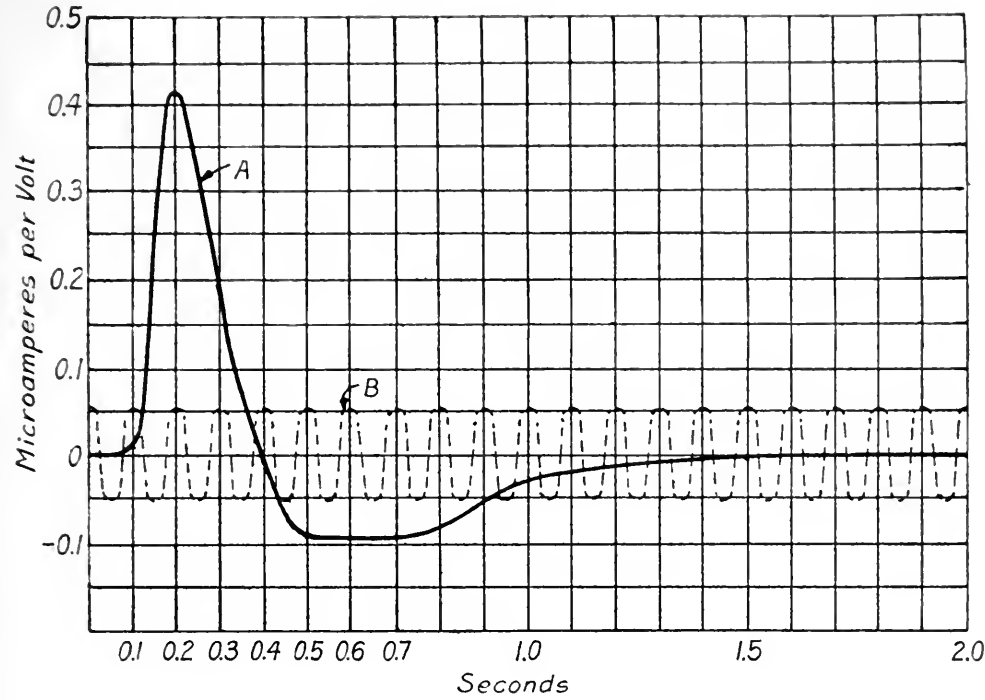


TABLE III.

$t(\text{secs.})$	0.1	0.2	0.3	0.4	0.5	0.7	1.0	1.5	2.0	3.0
$n = 1$	-0.4230	0.3371	0.2687	0.2140	0.1706	0.1085	0.0549	0.0177	0.0057	0.00066
$n = 2$	+3.3109	1.3362	0.5386	0.2183	0.0877	0.0143	0.0020	.....	.....	.....
$n = 3$	-4.9851	0.6494	0.0860	0.0075	.....	.....	.....	.....	.....	.....
$n = 4$	+2.6761	0.0750	.....	.....	.....	.....	.....	.....	.....	.....
$n = 5$	-0.6282	.....	.....	.....	.....	.....	.....	.....	.....	.....
$n = 6$	+0.0628	.....	.....	.....	.....	.....	.....	.....	.....	.....
Received Current, $I_r$	+0.0135	+0.4247	+0.1839	-0.0052	-0.083	-0.0942	- 0.035	-0.0117	-0.0057	-0.00066

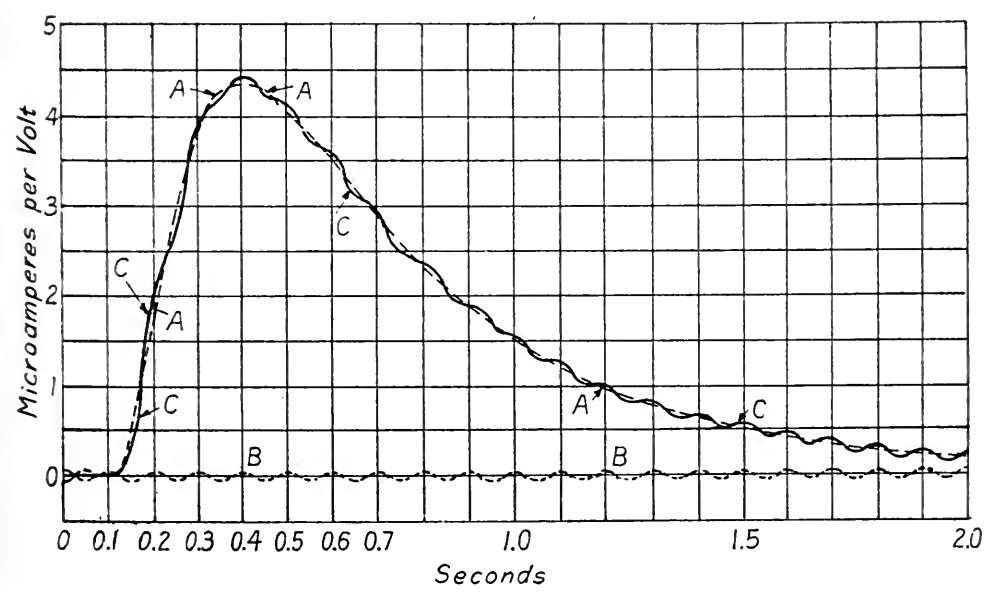


FIG. 1.



Arrival current, alternating e.m.f.  $n=10$ . Curve A—transient component.  
Curve B (broken)—periodic component.

FIG. 2.



Arrival current, alternating e.m.f.  $n=10$ . Curve A (broken)—transient component. Curve B (broken)—periodic component. C=total current.  $C=A+B$ .



## THE INFLUENCE OF TERMINAL APPARATUS.

Assume impedances  $Z_t$  and  $Z_r$  connected at the transmitting and receiving ends of the cable, respectively; the terminal conditions in this case are

$$\left. \begin{aligned} \text{for } x = 0, V &= E\epsilon^{j\omega t} - Z_t I_o, \\ \text{" } x = l, V &= Z_r I_l. \end{aligned} \right\} \quad (31)$$

Substituting these values in equations (4) and (5) the constants  $A$  and  $B$  are determined as follows:

$$\left. \begin{aligned} A &= \frac{E \left(1 - \frac{Z_r q}{R}\right) \epsilon^{-ql}}{\left(1 + \frac{Z_t Z_r}{R^2} q^2\right) (\epsilon^{-ql} - \epsilon^{ql}) - \frac{q}{R} (Z_t + Z_r) (\epsilon^{ql} + \epsilon^{-ql})}, \\ B &= \frac{-E \left(1 + \frac{Z_r q}{R}\right) \epsilon^{ql}}{\text{Same denominator}} \end{aligned} \right\} \quad (32)$$

and

$$I = \frac{E \frac{q}{R} \left\{ \left(1 - \frac{Z_r q}{R}\right) \epsilon^{-q(l-x)} + \left(1 + \frac{Z_r q}{R}\right) \epsilon^{q(l-x)} \right\} \epsilon^{j\omega t}}{\left(1 + \frac{Z_r Z_t}{R^2} q^2\right) (\epsilon^{ql} - \epsilon^{-ql}) + \frac{q}{R} (Z_t + Z_r) (\epsilon^{ql} + \epsilon^{-ql})}. \quad (33)$$

For  $x = l$  the received current is given by

$$I_r = \frac{E \epsilon^{j\omega t}}{\left(\frac{R}{q} + Z_r Z_t \frac{q}{R}\right) \sinh ql + (Z_t + Z_r) \cosh ql}. \quad (34)$$

For the steady state, the periodic component, replacing  $p$  by  $j\omega$  in the  $q$  expression ( $q = \sqrt{RCp}$ ), equation (34) is the solution. To get the complete solution to the problem, the transient as well as the periodic components, it is simplest to apply the Heaviside Expansion Theorem. In a paper published in the December issue of this JOURNAL<sup>4</sup> I have given the derivation of the Heaviside Expansion Theorem, extended to apply to a sinusoidal e.m.f. as well as a constant e.m.f. The theorem as formulated by Heaviside applies only to constant e.m.f. The formula derived from sinusoidal e.m.f. is as follows:

$$I = \frac{E \epsilon^{j\omega t}}{Z(p) \text{ } p=j\omega} - \sum_{p_1}^{p_m} \frac{\epsilon^{p_n t}}{(j\omega - p_n) \frac{\partial Z(p)}{\partial p} \text{ } p=p_n}. \quad (35)$$

<sup>4</sup> "The Heaviside Expansion Theorem," JOURNAL FRANKLIN INSTITUTE, Dec., 1922.



The first term of the right-hand side of the above equation gives the periodic component of the current and the summation term the transient component. The summation is to be extended to all the roots of the determinantal equation,

$$Z(p) = 0. \quad (36)$$

Doctor Malcolm utilizes the same method in getting the solution to this problem, but he made the serious error in applying the expansion formula as given by Heaviside for a constant e.m.f. to the condition of sinusoidal e.m.f. He modified the formula arbitrarily by the factor  $\frac{1}{\frac{\omega C R l^2}{p^2} + \frac{p^2}{\omega C R l^2}}$  for which there does not seem to be any foundation in theory. His conclusions therefore in this case are of course wrong. The difference in the final results in any practical case will be shown by the following consideration of one special case.

Take the case worked out by Malcolm, condensers of the same size at each end of the cable,

$$Z_l = Z_r = \frac{1}{C_0 p}.$$

Substituting in (34)

$$I_r = \frac{E \varepsilon^{j\omega t}}{\left(\frac{R}{q} + \frac{q}{RC_0^2 p^2}\right) \sinh ql + \frac{2}{C_0 p} \cosh ql} \quad (37)$$

The determinantal equation for this case is

$$Z(p) = \left(\frac{R}{q} + \frac{q}{RC_0^2 p^2}\right) \sinh ql + \frac{2}{C_0 p} \cosh ql = 0 \quad (38)$$

Remembering that  $q = \sqrt{RCp}$ , we have on differentiating with respect to  $p$

$$\begin{aligned} \frac{\partial Z(p)}{\partial p} &= \left(\frac{R}{\sqrt{RCp}} + \frac{\sqrt{RCp}}{RC_0^2 p^2}\right) \frac{\sqrt{RC} l}{2\sqrt{p}} \cosh \sqrt{RCp} l - \frac{1}{2\sqrt{p}} \left\{ \frac{R}{\sqrt{RCp}} + \frac{3\sqrt{RC}}{RC_0^2 p^2} \right\} \\ &\quad \cdot \sinh \sqrt{RCp} l + \frac{1}{C_0 p} \frac{\sqrt{RC} l}{\sqrt{p}} \sinh \sqrt{RCp} l - \frac{2}{C_0 p^2} \cosh \sqrt{RCp} l \\ &= \frac{1}{2p} \left\{ Rl + \frac{Cl}{C_0^2 p} - \frac{4}{C_0 p} \right\} \cosh \sqrt{RCp} l \\ &\quad - \frac{1}{2p\sqrt{p}} \left\{ \frac{R}{\sqrt{RC}} + \frac{3\sqrt{RC}}{RC_0^2 p} - \frac{2\sqrt{RC} l}{C_0} \right\} \sinh \sqrt{RCp} l. \end{aligned} \quad (39)$$

By (38) we have

$$\cosh \sqrt{RCp} l = -\frac{C_0 p}{2} \left( \frac{R}{\sqrt{RCp}} + \frac{\sqrt{RCp}}{RC_0^2 p^2} \right) \sinh \sqrt{RCp} l,$$



substituting in (39), combining and rearranging,

$$\frac{\partial Z(p)}{\partial p} = \frac{1}{\sqrt{RCpl}} \left\{ -\frac{C_0 R^2 l^2}{4} + \frac{1}{2} \frac{Rl}{p} - \frac{C^2 l^2}{4C_0^3 p^2} - \frac{1}{2} \frac{Cl}{C_0^2 p^2} + \frac{1}{2} \frac{RCl}{C_0 p} \right\} \sinh \sqrt{RCpl}. \quad (40)$$

The value of  $\frac{\partial Z(p)}{\partial p}$  given by above equation to be used in (35), assigning to  $p$  the values determined by (38).

As a practical illustration assume  $C_0 = \frac{1}{10} Cl$ , equation (40) reduces to

$$\frac{\partial Z(p)}{\partial p} = \frac{-Cl}{\sqrt{RCpl}} \left\{ \frac{R^2 l^2}{40} + \frac{300}{C^2 l^2 p^2} - \frac{5.5}{Clp} \right\} \sinh \sqrt{RCpl}. \quad (41)$$

To determine the roots of equation (38), we have

$$\tanh ql = \frac{-2}{C_0 p \left( \frac{R}{q} + \frac{q}{RC_0^2 p^2} \right)}, \quad (42)$$

put  $ql = jx$ ,  $RCpl^2 = -x^2$  and  $p = \frac{-x^2}{RCl^2}$ ,

equation (42) reduces to

$$\tan x = \frac{2Cl}{C_0 \left( x - \frac{C^2 l^2}{C_0^2 x} \right)},$$

and for

$$C_0 = \frac{1}{10} Cl$$

$$\tan x = \frac{20}{x - \frac{100}{x}} \quad \dots \quad (43)$$

The first eight roots of the above equation and the corresponding values of  $p$  are as follows:

$x$  2.6272, 5.307, 8.067, 10.909, 13.819, 16.782, 19.786, 22.817  
 $p$  -1.586, -6.462, -14.951, -27.345, -43.88, -60.14, -87.67, -119.65

By (35) we have for the transient component received current

$$I_t = \sum_{p_1}^{p_m} \frac{\epsilon^{p_n t}}{(j\omega - p_n) \frac{\partial Z(p)}{\partial p}} \quad p = p_n$$

The real part of above equations is

$$I_t = - \sum_{p_1}^{p_m} \frac{p \epsilon^{p_n t}}{(\omega^2 + p_n^2) \frac{\partial Z(p)}{\partial p}} \quad p = p_n$$

For the values of  $p$ , the roots of equation (38) given above, the following table was calculated.



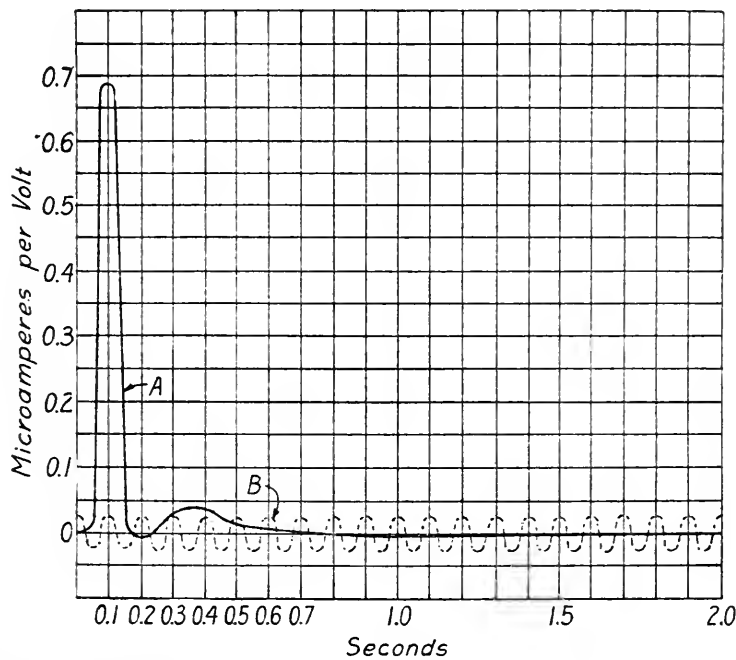
TABLE IV.

$p$	$\frac{p}{\omega^2 + p^2}$	$\frac{\partial z(p)}{\partial p}$	$\frac{p}{(\omega^2 + p^2)} \frac{\partial z(p)}{\partial p}$
-1.586	-0.0004	+28285	$-0.0141 \times 10^{-6}$
-6.472	-0.00162	-2022	$+0.801 \times 10^{-6}$
-14.951	-0.00358	+473	$-7.568 \times 10^{-6}$
-27.345	-0.00582	-140.7	$+41.364 \times 10^{-6}$
-43.88	-0.00747	+92.3	$-80.93 \times 10^{-6}$
-60.14	-0.00795	-61.2	$+129.9 \times 10^{-6}$
-87.67	-0.00753	+29.61	$-254.4 \times 10^{-6}$
-119.65	-0.00655	-18.24	$+359.0 \times 10^{-6}$

The values of  $\epsilon^{pt}$  for different time intervals are tabulated below in Table V.

Multiplying the values given in Table V by the values given in last column of Table IV, Table VI is constructed in which the

FIG. 3.



Arrival current, alternating e.m.f.  $n=10$ . Curve A-transient component. Curve B(broken)-periodic component.

values of the transient current component are given. The values are in microamperes per volt.

The steady current component can be readily calculated by formula (37) replacing  $p$  by  $j\omega$  and taking the real part thereof.







TABLE VI.

<i>t</i> (secs.)	0.1	0.15	0.2	0.3	0.4	0.5	0.7	1.0	1.5	2.0	3.0
$p = -1.586$	-0.0120	0.0111	0.0103	0.00876	0.00748	0.0064	0.00465	0.00289	0.00130	0.0006	0.00012
$p = -6.472$	+0.419	0.3036	0.220	0.1149	0.0602	0.0315	0.00863	0.00124	0.00005	.....	.....
$p = -14.951$	-1.697	0.8037	0.381	0.0853	0.0191	0.0043	0.00021	.....	.....	.....	.....
$p = -27.345$	+2.684	0.6825	0.174	0.0113	0.0007	0.00004	.....	.....	.....	.....	.....
$p = -43.88$	-1.003	0.1117	0.0125	0.00015	.....	.....	.....	.....	.....	.....	.....
$p = -60.14$	+0.325	0.0156	0.0008	.....	.....	.....	.....	.....	.....	.....	.....
$p = -87.67$	-0.0396	0.0742	.....	.....	.....	.....	.....	.....	.....	.....	.....
Received Current, $I_r$	+0.676	-0.0010	-0.0090	+0.032	+0.0443	+0.0208	+0.00377	-0.00165	-0.00125	-0.0006	-0.0001
Malcolm's values same example	-0.021	+0.189	+0.421	+0.435	+0.213	+0.039	-0.099	-0.101	-0.051	-0.023	-0.005



For a frequency of ten cycles per second the amplitude of the periodic component of the current thus calculated is 0.025 micro-ampere per volt.

The calculated values given in Table VI are shown in graphical form by the curves of Fig. 3.

The discussion in this paper was limited to a consideration of fundamental principles; it is highly important of course that we should have first of all a correct theory of the subject. The application of the theory developed here to some special problems in cable telegraphy, will be considered in another paper. I have in mind particularly the problem of signalling either by the method of resistance variation proposed by General Squier or the method of varying the length of cable cutting in or out sections of artificial cable proposed by the writer.<sup>5</sup> It is believed that these methods offer particular advantages in the alternating current system of cable telegraphy.

---

**The Use of a Triode Valve in Registering Electrical Contacts.**  
G. A. TOMLINSON. (*Phil. Mag.*, Nov., 1922.)—"A three-electrode valve can be applied with advantage to certain forms of apparatus in which use is made of electrical contacts. A common case is that of a relay in which it is usual to cause a feeble movement of one instrument to make a contact and close the circuit of a second comparatively powerful instrument supplied from an independent source. An improvement in several respects can be made if the first contact is placed in the grid circuit of a valve, and the second instrument is connected in the anode circuit and is operated by the anode current." For a relay of this type several advantages are claimed. The current through the contact points is small, being merely the grid current. Resistance at the points need not be always the same because there is in circuit the large resistance from grid to filament. "A further advantage, that may be important in some cases, is that this relay may be operated by much weaker forces than could be used with an ordinary relay. . . . It has been found that a contact force of 0.000001 grm. is quite sufficient to charge the grid and produce the required change in the anode current." In making exact measurements of thicknesses or distances electrical means are often used to determine the fact of contact. When the triode valve was employed for this purpose "it was found that repetition of observations could easily be obtained with variations not exceeding  $0.5^{-6}$  inch." It is suggested that the method may be used for the reception of very feeble wireless signals.  
G. F. S.

---

<sup>5</sup> U. S. Patent No. 1,414,179, April 25, 1922.



# A SURVEY OF EXISTING CRYSTAL STRUCTURE DATA.\*

BY

RALPH W. G. WYCKOFF, Ph.D.

Physical Chemist, Geophysical Laboratory, Carnegie Institution of Washington.

## INTRODUCTION.

THE use of information furnished by the theory of space-groups in studying the arrangement of atoms in crystals has made possible a completely new attitude towards crystal structure results. Hitherto it was necessary to be content with the determination of a possible structure which would account for a few limited data taken in a haphazard fashion. Space-group results permit the detailed consideration of all of the atomic arrangements possible for a crystal and offer the opportunity of choosing the experimental data in such a manner that they will select the correct structure.

The results thus obtained are of a different order of value from those derived by the older procedure: In the one case a structure is achieved which may be the correct one; in the other, either a unique solution is deduced or else the several structures which remain possibilities are each of them completely known. In the earlier days any information concerning the internal construction of crystals was very properly treasured but now, when it is not necessary to be content with results of an uncertain character, there hardly remains the same justification for their accumulation.

Since there is such great difference between the worth of studies of crystal structure carried out by these two different procedures and since most of the work that has been and still is being done proceeds from the older point of view, a survey of existing crystal structure data is urgently needed. This paper aims in part to provide such a discussion. Most of the older determinations have not been checked up as yet. Many of them are of very simple crystals with a large probability of correctness. In judging the value of these studies, then, the element of personal

---

\*Communicated by Dr. Arthur L. Day, Director of the Geophysical Laboratory and Associate Editor of this JOURNAL.



judgment must necessarily be introduced, and allowed for, though it distinctly is not involved in comparative discussions of work carried out by the older and newer methods. Eventually all of the old determinations must be more or less thoroughly reworked from the standpoint of space-group theory; for this reason its earliest possible introduction is greatly to be desired.

In the accompanying tabulations the various determinations of structure are placed in the following classification: Class I, those structures which have been obtained with the aid of space-group results; Class II, those studied by the older methods; Class III, the few investigations which have been adequately carried through from a theoretical standpoint but which either are based upon insufficient data or on data which are in radical disagreement with the results of apparently equally good experimentation. Both Classes I and II are made subject to a further division:

Class IA, studies in which all possible arrangements have been considered.

Class IB, determinations in which space-group data have been used to pick out a structure but not to define all that may be possible. To this group belong the early investigations which used space-group information together with a few studies of crystals of relatively low symmetry.

Class IIA, possible atomic arrangements which in spite of the incompleteness of their determination the present writer considers to be almost certainly correct.

Class IIB, all other studies of crystal structure.

Not only must the value of determinations of structure be judged from the character of the general procedure used, but account must also be taken of the nature of the experimental data upon which they are based. This is especially true in a weighing of structures that must be assigned to Class II; for, while determinations based upon a proper use of the results of the theory of space-groups may be incomplete or inconclusive because of a lack of the proper data, they never will be indefinite. On the contrary, it frequently happens that the data underlying determinations of atomic arrangement by the older methods are of such a character as to make them little more than guesses.

At the present time there are four commonly employed methods of obtaining diffraction data from crystals. In weighing the value of these various methods for crystal structure work it



is necessary to consider not only the amount, but also the usefulness of the data supplied. Because of the lack of exact knowledge of the laws of scattering for X-rays, it is now necessary to employ a relatively large number of qualitative considerations in place of a few quantitative measurements. Laue photographs, in making easily available a large amount of such qualitative information, form the most valuable single method of collecting data. Of the others, powder experiments yield the most data by furnishing together reflections from planes of many crystal forms. At the same time this very advantage may present, especially in the case of crystals of low symmetry, an uncertainty in the correct choice of indices of observed reflections. The powder method has furthermore been commonly used to study the structures of substances which do not crystallize well. Such material is often contaminated with crystalline impurity which will itself give diffraction lines. There is consequently a great temptation to ascribe any reflections which are incompatible with a simple structure to this impurity. The dangers that may arise from this source are evident. The other two methods of producing diffraction phenomena, as is well known, consist in reflecting X-rays from single crystal faces: In the original Bragg experiment the positions and relative intensities of the reflections are recorded by an ionization chamber method; in the other case a photographic plate is used. The first of these, the spectrometer method, is open to grave error because unless particular care is taken reflections from faces other than the one supposedly under investigation may get into the detecting chamber and give either false readings of intensity or entirely new, and spurious, reflections.

The satisfactory method of experimentation has at hand all four of these means of accumulating diffraction data and uses those which are best adapted to the collection of the information required to establish the structure in hand. This procedure as yet has been followed only in relatively few instances.

Unfortunately an investigator often has become a devotee of some one method of collecting diffraction data and has applied it to the exclusion of all other procedures. This has been particularly true of the powder method and of the spectrometer method used as a basis of determinations which did not avail themselves of space-group information. The inadequacy of such



a method of approach to problems of crystal structure is shown in its results. A number of the more striking and conclusive illustrations of insufficiency are collected in the conclusion to this paper. In view of these practical examples of the breakdown of the older method of procedure and of the failure of any one method of collecting data to serve as a panacea for all crystal structure difficulties, it seems hardly necessary to point out again the necessity of a wider and less prejudiced use of all of the additional information which is available both from the theory of space-groups and from the conventional crystallography.

It may quite naturally be supposed that the unique character of a determination can be established for many Class II studies by a simple reworking of the original data. It happens, however, that most of the crystal structure papers published in this country contain no fundamental measurements. The responsibility for this does not rest entirely with the authors of these papers for conditions of publication have not permitted the printing of an adequate number of the experimental data upon which assignments of structure are based. This condition, over which crystal analysts themselves have only a relatively slight and indirect influence, is unfortunate in putting American writers at a serious disadvantage compared with their European co-workers. Economic circumstances, though, appear now to have so far adjusted themselves that it is no longer, if indeed it ever was, necessary to go to the extreme of reporting results without data of any sort. This in itself is a reason for rejoicing because a large number of the structures emanating from this country have appeared in this scant fashion, and it is certain that their ultimate fate must be to be completely disregarded. Continued improvement in opportunities for publication is a necessity for the welfare of crystal structure work, and it must be hoped that the time is not too far distant when structure determinations can be properly presented, and in English.

Very few of the determinations of crystal structure furnish any assurance, either by direct or indirect analysis, of the purity or even of the composition of the material under investigation. Methods have now so far developed that carefully made observations upon diffraction effects may be expected to have more than the transitory value of the earliest measurements. Thus there is no longer a reason for the disregard of so vital a factor



in the determination of the structure of a crystal as some knowledge of its actual composition.

Many studies of X-ray diffraction effects from crystalline materials have been made for purposes other than the direct study of atomic arrangements. They will not receive attention in the present review.

For order in presentation and ease of reference crystal structure investigations must be grouped according to some scheme which not only will include those now available, but will be sufficiently elastic to accommodate future work. For this purpose a system which has found general use in the classification of crystals themselves may naturally be followed. That used by Dana,<sup>1</sup> or the closely similar one of Groth,<sup>2</sup> particularly commend themselves by their completeness. In so far as they differ from one another, that of Groth is perhaps the more arbitrary, but it has the overwhelming advantage of including organic as well as inorganic crystals. Its major outline, for the crystals whose structures have been studied, is shown in Table I. A deviation from this classification in the discussion of individual crystals will, however, be made wherever it may prove convenient.

TABLE I.

*The Order of Discussion of Crystal Structures.*

Elements.

Inorganic compounds not salts.

Alloys, etc.

Carbides, etc.

Oxides.

Hydroxides.

Sulfides, selenides, etc.

Halides, cyanides, etc.

Anhydrous compounds.

Polyhalides.

Double (and triple) halides and cyanides.

Nitrates, chlorates, bromates, etc.

Simple compounds.

Hydrates and ammonates.

Carbonates.

Silicates, titanates, etc.

Sulfates, chromates, manganates, etc.

Borates, aluminates, ferrites, etc.

Organic compounds.

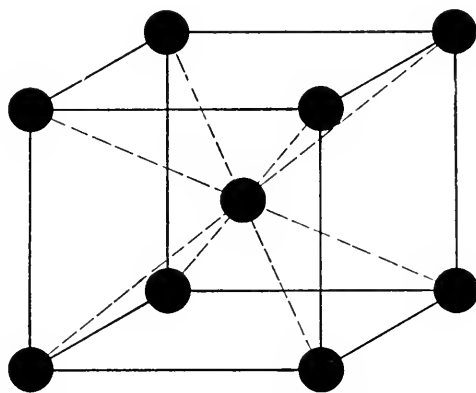


## THE CRYSTAL STRUCTURES OF THE ELEMENTS.

## THE METALS OF THE FIRST VERTICAL GROUP.

THE ALKALI METALS.—All work on the alkali metals has been carried out by the powder method. These metals are said to crystallize with a difficulty which becomes greater with increase in the atomic weight of the metal; the powder data consequently are rather meagre and quite insufficient for a thoroughly satisfactory determination. Considered, however, in connection with the structures of the better studied metals, it seems highly probable that the arrangements assigned to these metals are correct. The unit cube of each contains two atoms. This arrangement, which may be described as one that places one atom at each point

FIG. 1.



The unit cube of the body-centred arrangement of atoms in elements. The coördinate positions of the equivalent atoms in this unit are:  $000$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

of a body-centred space lattice, is shown in Fig. 1. The coördinate positions of the atoms within the unit are:

$$000; \quad \frac{1}{2}\frac{1}{2}\frac{1}{2}.$$

*Lithium*.—Two investigations of lithium have been made. Early data<sup>3</sup> indicated that the arrangement was probably that of a body-centred cube 3.50A.U. on a side; subsequent measurements<sup>4</sup> are in agreement with such a structure having the same dimensions.

*Sodium*.—Considerable difficulty was experienced in preparing crystalline sodium and the best obtainable photographs were darkened by the presence of quantities of amorphous metal. The relatively few lines found are said to agree in position with those of a body-centred cube<sup>3</sup> of side  $a = 4.30\text{A.U.}$

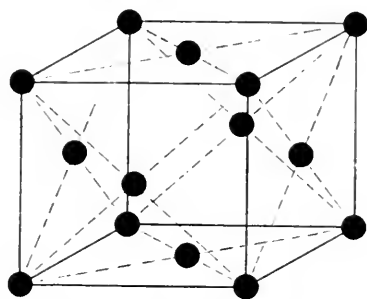
*Potassium*.—An attempt<sup>3</sup> to prepare potassium at room temperature which would give any diffraction pattern failed. Such



a pattern has been obtained<sup>5</sup> at  $-150^{\circ}$  C., but all evidence of crystallinity had vanished at  $-20^{\circ}$  C. The diffraction results observed at  $-150^{\circ}$  C. by a slow rotation through small angles are considered to agree best with a body-centred structure 5.20A.U. on a side. No data are published by which the value of this assignment of structure may be gauged.

THE SUB-GROUP ELEMENTS.—Diffraction measurements have been made upon all three metals: Copper, silver and gold. With the exception of some powder measurements incidental to a study of sputtered films all data have been obtained from spectrometric observations upon not more than three crystal faces. All agree in assigning an arrangement which places one atom at

FIG. 2.



The face-centred arrangement of the atoms in elements. The coördinate positions of four equivalent atoms within the unit are:  $000$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

each point of a face-centred cubic lattice (Fig. 2). The coördinates of the typical atomic positions within the unit cube are thus:

$$000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}.$$

In spite of the insufficiency of the data it is probable that these assignments are correct.

*Copper*.—Reflections were obtained<sup>6</sup> from the (100), (110) and (111) faces of a natural crystal. The length of the side of the unit containing four atoms was determined as:  $a = 3.60\text{A.U.}$

*Silver*.—Similar spectrometer measurements<sup>7</sup> have been recorded for natural crystals of silver. The length of the side of the unit:  $a = 4.06\text{A.U.}$  It also has been stated that powder measurements<sup>8</sup> are in agreement with a face-centred structure of the same size, but no data are given.

*Gold*.—Only a reflection from an octahedral face was obtained. From this<sup>9</sup> the length of the side of the unit cube:  $a = 4.07\text{A.U.}$  Powder measurements (no data supplied)<sup>8</sup> are

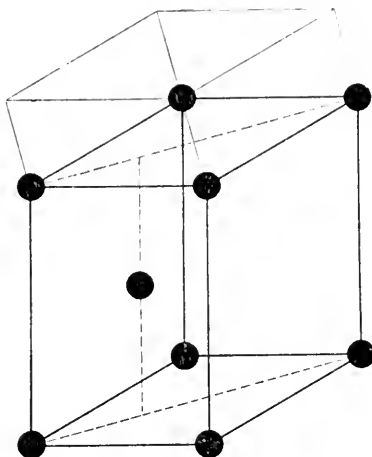


said to agree with a face-centred arrangement having a unit 4.08A.U. on a side.

#### THE METALS OF THE SECOND VERTICAL GROUP.

THE TRANSITIONAL ELEMENTS BERYLLIUM AND MAGNESIUM.—Both of these metals crystallize in the hexagonal system. Primarily on the ground of powder data they have been assigned an atomic arrangement which is a near approach to the closest

FIG. 3.



The close-packed hexagonal arrangement of the atoms in elements. The coördinate positions of the two equivalent atoms within this unit cell are:  $000$ ;  $\frac{1}{3}, \frac{2}{3}, u$ . Unless the crystal possesses holohedral symmetry the parameter  $u$  will not be exactly  $\frac{1}{2}$ . The hexagon completed by the light lines at the top of the figure serves to show the relation of this unit cell to the large hexagonal prism.

packing of solid spheres. This structure, shown in Fig. 3, has atoms in the coördinate positions:

$$000; \quad \frac{1}{3}, \frac{2}{3}, u.$$

The powder data do not seem capable of establishing the precise value of  $u$ . Other possible structures are taken account of only for magnesium. In no case, however, is a treatment given which is based upon space-group theory. A more complete study of one of these metals would be desirable, particularly if it could be obtained in crystals large enough for Laue photographic measurement.

*Beryllium.*—This structure was assigned<sup>10</sup> to powdered beryllium in stating the arrangement as two interpenetrating hexagonal lattices, the exact manner of intermeshing of which could not be determined with accuracy. The length of the side of the unit cell containing two atoms (as illustrated in Fig. 3):  $a$  (the base) = 2.283A.U.;  $c$  (the height) = 3.607A.U. The result-



ing axial ratio is in agreement with the crystallographically determined  $c : a = 1.580$ .

*Magnesium*.—Magnesium has been given the structure already discussed on the basis of powder data and spectrographic data obtained<sup>3, 11</sup> by recording reflections from the basal section of a single crystal. The dimensions of the unit cell:  $a = 3.22 \text{ A.U.}$ ;  $c = 5.23 \text{ A.U.}$  The results using a modified form of powder spectrograph<sup>12</sup> are considered to be in agreement with a structure built up of two interpenetrating hexagonal lattices, the units of which each have the dimensions:  $a = 3.23 \text{ A.U.}$ ;  $c = 5.25 \text{ A.U.}$  This is equivalent to the one already described. Though the manner of interpenetration of these lattices, that is, the value of  $u$ , could not be determined, these data are held not to be compatible with  $u = \frac{1}{2}$ .

THE ALKALINE EARTH METALS.—*Calcium* has been studied. Powder photographic data<sup>27, 13</sup> are believed to point to a face-centred cubic arrangement (Fig. 2). A comparison photograph of calcium oxide was prepared in order to eliminate its lines from the spectrum of metallic calcium. The length of the side of the unit cube containing four atoms:  $a = 5.56 \text{ A.U.}$

THE SUB-GROUP ELEMENTS ZINC, CADMIUM AND MERCURY.—Powder diffraction data have been used to assign crystal structures to all three of these metals. Following the same general mode of procedure, the same closest-packed arrangement has been given to the first two as to magnesium. Crystalline mercury does not appear to have this structural arrangement and will be discussed separately.

*Zinc*.—The powder data<sup>19</sup> are considered to be in agreement with a unit cell for which  $a = 2.670 \text{ A.U.}$  and  $c = 4.966 \text{ A.U.}$  As with the other metals crystallizing similarly the possibility of the parameter  $u$  being other than one-half has not been considered. The axial ratio corresponding to this unit,  $c : a = 1.860$ , is not in agreement with the crystallographically determined ratio,  $c : a = 1.356$ . Whatever the explanation of this discrepancy may be, it is clear that a further study of zinc will be profitable.

*Cadmium*.—The same dilemma exists with respect to the axial ratio of cadmium crystals. The X-ray powder data<sup>19</sup> are considered to agree with a unit cell for which  $a = 2.980 \text{ A.U.}$  and  $c = 5.632 \text{ A.U.}$  The corresponding axial ratio is  $c : a = 1.89$  as contrasted with the crystallographically determined 1.335.



*Mercury*.—Powder photographs have been used to establish two different structures for crystals of mercury. The results of one study<sup>15</sup> are said to be in agreement with a grouping of the mercury atoms at the corners of a simple rhombohedron for which  $a = 3.025 \text{ A.U.}$  and  $\alpha$  (the angle between the axes)  $= 70^\circ 31.7'$ ; this is said to correspond in terms of hexagonal axes to  $a = 3.493 \text{ A.U.}$  and  $c : a = 1.9365$ . The hexagonal equivalent of a simple rhombohedral arrangement contains three atoms within the unit cell. In this paper no other possible atomic groupings are treated. The other hexagonal structure<sup>16</sup> places four atoms within the unit cell. After a treatment of the various arrangements with this number of atoms in the unit which the results of the theory of space-groups suggest, an arrangement is chosen which places mercury atoms in the coördinate positions:  $000$ ;  $0, 0, u + \frac{1}{2}$ ;  $2/3, 1/3, \frac{1}{2}$ ;  $2/3, 1/3, u$ , where the value of the parameter  $u$  was not determinable. The measurements of the first paper were taken at  $-115^\circ \text{ C.}$ , those of the second at the temperature of carbon dioxide snow. Both determinations have practically the same value for the axial ratio, and it may be doubted if the explanation of the conflict between these two studies lies in the existence of two modifications of mercury. A reworking of these data is urgently needed. In the meantime any decision as to their probable correctness must be held in abeyance, though from a theoretical standpoint the second<sup>16</sup> determination is incomparably better done.

#### THE METALS OF THE THIRD VERTICAL GROUP.

Only two metals of this group have been studied: Aluminum and indium. Both have been examined only with powder data without any treatment making use of the results of the theory of space-groups.

*Aluminum*.—Two independent determinations<sup>3, 17, 18</sup> of the structure of metallic aluminum assign a face-centred cubic arrangement (Fig. 2) to its atoms. These two studies place the side of the unit cube:  $a = 4.05 \text{ A.U.}$ <sup>3</sup> and  $a = 4.07 \text{ A.U.}$ <sup>18</sup>

*Indium*.—Powder photographic data from indium<sup>19</sup> are said to be in agreement with an arrangement of its atoms at the points of a face-centred tetragonal lattice of axial ratio  $c : a = 1.06$ . The lengths of the edges of this unit are  $a = 4.58$ -

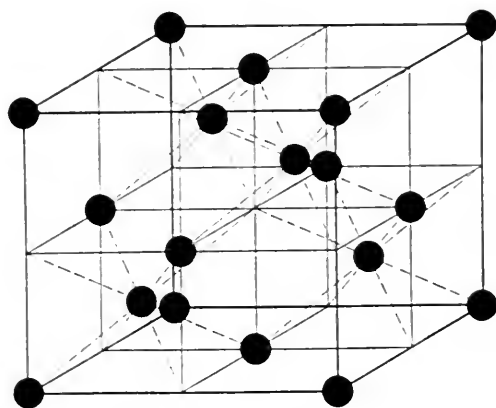


A.U.,  $c = 4.86$  A.U. No other tetragonal structure which might be in agreement with these data has been considered.

#### THE ELEMENTS OF THE FOURTH VERTICAL GROUP.

THE TRANSITIONAL ELEMENTS CARBON AND SILICON.—The crystal structure of carbon in various physical states has been studied. All of the diffraction patterns thus obtained, with the exception of the one from diamond, are identical with that exhibited by graphite. Laue photographs, spectrometer measurements and powder data have all been examined in the light of more recent procedure. Powder data have been used by

FIG. 4.



The "diamond" type of arrangement of the atoms of elements. The coördinate positions of the eight equivalent atoms within the unit are:  $000$ ;  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ .

two sets of observers to assign two totally different structures to graphite.

Several measurements, all of which give it the diamond structure, have been made of the powder reflections from silicon.

*Carbon.*—The coördinate positions of the atoms of carbon within the unit cube of the diamond according to the accepted structure are as follows (Fig. 4):

$$000; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}.$$

The length of the side of this unit cube, as determined by the original spectrometric measurements<sup>20, 85</sup> is  $3.55$  A.U. The recorded powder data<sup>3</sup> give practically the same value:  $a = 3.56$  A.U.

Before the time of X-ray methods of investigation the symmetry of graphite was in doubt. A Laue photograph,<sup>21</sup> as well as all of the powder data and the most reliable crystallographic indications, make it hexagonal. One set of powder data<sup>22, 23</sup> is thought to be in agreement with a rhombohedral structure of



considerable complexity of atomic arrangement. The other set<sup>3, 24</sup> is held to disagree with this structure and to establish one that is hexagonal. Graphite presents another case of the ease with which powder photographic data can go astray in the determination of the structures of any but the simplest crystals when unaided by definite crystallographic information. Not only is further work necessary for the reconciling of these conflicting results, but it is imperative that the results of space-group theory be invoked in the discussion of all possible arrangements before any structure can be accepted for graphite.

*Silicon.*—Three assignments<sup>3, 17, 25, 26</sup> of structure based upon powder data all give silicon the diamond arrangement (Fig. 4). They yield the following lengths of the side of the unit cube:  $a = 5.46\text{A.U.}$ ,  $5.40\text{A.U.}$ ,  $5.43\text{A.U.}$ , with the last most probably correct.

THE FIRST SUB-GROUP ELEMENTS OF THE FOURTH GROUP  
TITANIUM, ZIRCONIUM, CERIUM AND THORIUM.—The structures of all of these metals have been investigated with powder photographs without a treatment based upon the results of the theory of space-groups. The diffraction data for the first three are considered to agree with a close-packed hexagonal arrangement analogous to that found for magnesium (Fig. 3). No account is taken of the possibility of the parameter  $u$  which defines the  $z$  coördinate of the second atom within the unit cell being other than one-half. For this reason, even if these structures are essentially correct, the interatomic distances calculated from them cannot be taken as more than approximate. Two independent determinations of thorium assign it to the closely related cubic close-packed arrangement (Fig. 2). Cerium is said probably to have a second cubic modification which is like thorium and can exist along with the hexagonal structure. No data have as yet been published for any of these studies except one on thorium.<sup>12</sup>

*Titanium.*—The dimensions<sup>27, 28</sup> of the unit cell:  $a = 2.97\text{A.U.}$ ;  $c = 4.72\text{A.U.}$ , corresponding to the axial ratio  $c:a = 1.59$ .

*Zirconium.*—The dimensions<sup>28</sup> of the unit cell:  $a = 3.23\text{A.U.}$ ,  $c = 5.14\text{A.U.}$ , corresponding to the axial ratio  $c:a = 1.59$ .

*Cerium.*—Cerium<sup>28</sup> is probably dimorphous, crystallizing in both the hexagonal and cubic close-packed arrangements. The dimensions of the hexagonal unit are stated as:  $a = 3.65\text{A.U.}$ ,



$c = 5.96\text{A.U.}$ , the axial ratio being  $c : a = 1.62$ . The cubic modification (Fig. 2) is reported to have a length of side of  $a = 5.12\text{A.U.}$

*Thorium*.—The two determinations<sup>28, 12</sup> of structure give the lengths of the sides of the unit cube (Fig. 2) :  $a = 5.04\text{A.U.}$  and  $5.12\text{A.U.}$ , respectively.

THE SECOND SUB-GROUP ELEMENTS OF THE FOURTH GROUP GERMANIUM, TIN AND LEAD.—Measurements have been made upon all three of these metals, the first two with the aid of powder photographs, the last by a single reflection from a (111) crystal face. Germanium and gray tin have been given the diamond arrangement (Fig. 4), white tin a tetragonal structure, and lead one that is face-centred cubic (Fig. 2).

*Germanium*.—Powder data<sup>24, 29</sup> are said to be in agreement with a diamond arrangement, the edge of the unit cube of which (Fig. 4) is  $5.63\text{A.U.}$  or  $5.61\text{A.U.}$  Data have been published only for the second determination.<sup>29</sup>

*Tin*.<sup>30</sup>—Gray tin is assigned the diamond arrangement (Fig. 4), the length of the side of the unit cube being :  $a = 6.46\text{A.U.}$  The unit of white tin is given as a tetragonal prism containing three atoms in the coördinate positions :  $000$  ;  $\frac{1}{2}0\frac{1}{2}$  ;  $0\frac{1}{2}\frac{1}{2}$ . The published dimensions of this unit are :  $a = 5.84\text{A.U.}$ ,  $c = 2.37\text{A.U.}$ , corresponding to the axial ratio  $c : a = 0.406$ . Apparently this study with powder photographic data offers only a possible atomic arrangement, at least until a complete treatment based upon the results of the theory of space-groups has been carried out.

*Lead*.—A single reflection<sup>9</sup> from a (111) face of a lead crystal is in agreement with a face-centred cubic unit (Fig. 2) for which the length of the unit side is :  $a = 4.91\text{A.U.}$  The need of more work upon this metal is obvious.

#### THE ELEMENTS OF THE FIFTH VERTICAL GROUP.

The structure of neither of the transitional elements has been studied. Two of the first sub-group elements, vanadium and tantalum, and two of the elements of the second sub-group, antimony and bismuth, have given diffraction data.

THE FIRST SUB-GROUP ELEMENTS OF THE FIFTH GROUP VANADIUM AND TANTALUM.—A body-centred cubic arrangement has been assigned to both of these metals on the basis of powder photographic data.

*Vanadium*.<sup>24</sup>—The length of the side of the unit cube con-



taining two atoms (Fig. 1) is given as  $a = 3.04\text{A.U.}$  No data have as yet been published.

*Tantalum*.<sup>27, 19</sup>—The length of the side of the unit (Fig. 1) is  $3.272\text{A.U.}$

THE SECOND SUB-GROUP ELEMENTS OF THE FIFTH GROUP  
ANTIMONY AND BISMUTH.—Both powder data and spectrometric measurements have been accumulated for bismuth while only spectrometric data are available for antimony. Both have the symmetry of the hexagonal system. The different structures that have been assigned to each of them offer another example of the results to be expected from the application of the older procedure of crystal structure study. Recent spectrometer measurements are in disagreement with the early structure which gave both antimony and bismuth a diamond arrangement<sup>34</sup> distorted along the trigonal axes so that the unit cubes became rhombohedrons. The later data agree in giving to the two elements a similar atomic marshalling, but the ratio of the intensities of reflection from the various orders from the (111) face, particularly in the case of antimony, are very different, so that the positions of the atoms are not the same in the two results. Powder photographic data for bismuth were thought to give evidence for still another atomic arrangement.

*Antimony*.—A detailed consideration of the existing determinations is not justified. The recently proposed structure is described as a rhombohedral one containing eight atoms within the unit cell: Four lying upon a face-centred arrangement possessing rhombohedral symmetry and the other four upon another similar arrangement which is displaced along the trigonal axes of the first by an amount which differs for the two observers.<sup>31, 32</sup>

*Bismuth*.—Bismuth has been given three structures. The original distorted diamond arrangement<sup>34</sup> is considered to have been disproved by the more recent spectrometric observations,<sup>32, 33</sup> which themselves are said to agree with a structure similar to the one assigned to antimony. The structure deduced from powder data<sup>8</sup> is a simple rhombohedral arrangement of bismuth atoms.

#### THE ELEMENTS OF THE SIXTH VERTICAL GROUP.

*The Transitional Element Sulfur*.—Spectrometric measurements<sup>35</sup> have been made upon crystals of orthorhombic sulfur. Especially when viewed in the light of the difficulties encountered



in deducing the structure of the simpler bismuth, for example, it must be clear that these observations are of little value towards establishing atomic arrangement in sulfur.

THE FIRST SUB-GROUP ELEMENTS OF THE SIXTH GROUP CHROMIUM, MOLYBDENUM AND TUNGSTEN.—All of these elements have been studied by the unaided powder method. They are said to be cubic with a body-centred arrangement of their atoms (Fig. 1).

*Chromium*.<sup>19</sup>—The unit cell (Fig. 1) has a length of side:  $a = 2.895A.U.$

*Molybdenum*.—Two determinations<sup>19, 36</sup> of the length of the edge of the unit cube give  $a = 3.143A.U.$  and  $3.08A.U.$ , respectively.

*Tungsten*.—The two studies<sup>37, 19</sup> of this structure place  $a = 3.18A.U.$  and  $3.150A.U.$ , respectively. The latter determination was based upon a comparison photograph of molybdenum and tungsten for which no data have been furnished.

THE SECOND SUB-GROUP ELEMENTS OF THE SIXTH GROUP.—No attempts have been made to determine the arrangement of the atoms in either selenium or tellurium crystals.

#### THE ELEMENTS OF THE SEVENTH VERTICAL GROUP.

No diffraction measurements have been made upon any element of this group.

#### THE ELEMENTS OF THE EIGHTH VERTICAL GROUP.

Structures, based upon powder photographic data, have been given to all of the metals of this group. Spectrographic measurements have also been made upon individual crystals of iron<sup>3</sup> containing about  $3\frac{1}{2}$  per cent. of silicon. The data from this alloy were in agreement with the powder data from pure iron. Of these metals, rhodium, palladium, iridium and platinum are given the face-centred cubic arrangement (Fig. 2); ruthenium and osmium the close-packed hexagonal grouping (Fig. 3); cobalt is said to crystallize in both of these forms which can coexist at ordinary temperatures;  $\alpha$ - and  $\beta$ -iron are body-centred cubic (Fig. 1), while  $\gamma$ -iron, stable at  $1000^{\circ}C.$ , is face-centred; and nickel, which at first was said to have coexistent body-centred and face-centred cubic structures, is now described only in the face-centred modification.



*Iron*.—Two determinations<sup>38, 3, 39, 40, 41</sup> of the structure of the low temperature form of iron place the length of the side of the unit cube containing two atoms (Fig. 1) at 2.86A.U. and 2.87A.U. The atomic arrangement of the  $\gamma$ -form<sup>40, 41</sup> at 1000° C. is given as face-centred (Fig. 2), the length of the edge of the unit cube being 3.60A.U.

*Nickel*.—As originally described,<sup>3</sup> nickel had both a face-centred and a body-centred modification. Subsequently it is stated<sup>19, 39</sup> that only the diffraction patterns of a face-centred cubic arrangement (Fig. 2) 3.540A.U. on a side could be found. The other study<sup>12</sup> of nickel also gives it a face-centred structure for which  $a = 3.53$ A.U.

*Cobalt*.<sup>39, 19</sup>—Two forms of cobalt can be prepared either practically free from one another or mixed in various proportions. For the face-centred cubic arrangement (Fig. 2)  $a = 3.554$ A.U.; the hexagonal close-packed possesses a unit with a base  $a = 2.514$ A.U. and an axial ratio  $c : a = 1.633$ . This axial ratio is precisely that of the closest packing of spheres.

*Ruthenium*.<sup>27, 19</sup>—The close-packed hexagonal unit (Fig. 3) has the dimensions:  $a = 2.686$ A.U.,  $c = 4.272$ A.U., corresponding to the axial ratio  $c : a = 1.59$ .

*Rhodium*.<sup>19</sup>—For the face-centred cubic structure (Fig. 2):  $a = 3.820$ A.U.

*Palladium*.<sup>27, 19, 42</sup>—Face-centred cubic (Fig. 2). Two determinations give  $a = 3.950$ A.U. and  $a = 3.90$ A.U. It has also been noted that when metallic palladium absorbs hydrogen, it swells several per cents. without other change in structure.

*Osmium*.<sup>28</sup>—Hexagonal close-packed arrangement (Fig. 3). The unit cell has the dimensions:  $a = 2.714$ A.U.,  $c = 4.32$ A.U., corresponding to the axial ratio  $c : a = 1.59$ .

*Iridium*.<sup>27, 19</sup>—Face-centred cubic arrangement (Fig. 2).  $a = 3.805$ A.U.

*Platinum*.<sup>27, 19, 8</sup>—Face-centred cubic arrangement (Fig. 2). Two determinations of the dimensions of this unit (the second upon sputtered films of metal) place  $a = 3.930$ A.U. and 4.02A.U., respectively.

#### SUMMARY OF THE STRUCTURES OF THE ELEMENTS.

Mention has now been made of the various attempts to determine the arrangement of the atoms in crystals of the chemical elements. The results of these studies are summarized in Table II.



Element.	System of Symmetry.	Type of Arrangement.	Text Figure of Unit Cell.	Dimensions of Unit Cell.	Class of Determination.
Lithium.....	Cubic	Body-centred	Fig. 1	$a = 3.50A. U.$	IIA
Sodium.....	Cubic	Body-centred	Fig. 1	$a = 4.30$	IIA
Potassium ( $\sim 150^\circ$ ) .....	Cubic	Body-centred	Fig. 1	$a = 5.20$	IIA?
Copper.....	Cubic	Face-centred	Fig. 2	$a = 3.60$	IIA
Silver.....	Cubic	Face-centred	Fig. 2	$a = 4.06$	IIA
Gold.....	Cubic	Face-centred	Fig. 2	$a = 4.07; 4.08$	IIA
Beryllium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.283; c = 3.607$	IIA
Magnesium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 3.23; 3.22; c = 5.25; 5.23$	IIA
Calcium.....	Cubic	Face-centred	Fig. 2	$a = 5.56$	IIA
Zinc.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.670; c = 4.966$	IIA
Cadmium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.980; c = 5.632$	IIA
Mercury.....	Hexagonal?	.....	.....	.....	IIA
Aluminum.....	Cubic	Face-centred	Fig. 2	$a = 4.05; 4.07$	IIA
Indium.....	Tetragonal	Diamond	Fig. 4	$a = 3.55; 3.56$	IIIB
C (diamond).....	Cubic	Diamond	.....	.....	IIA
C (graphite).....	Hexagonal	Diamond	Fig. 4	$a = 4.53; 4.50; 4.56$	IIIB
Silicon.....	Cubic	Diamond	Fig. 4	$a = 2.97; c = 4.72$	IIA
Titanium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 3.23; c = 5.14$	IIA
Zirconium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 3.65; c = 5.96$	IIA?
Cerium.....	Cubic	Face-centred	Fig. 2	$a = 5.12$	IIA?
Thorium.....	Cubic	Face-centred	Fig. 2	$a = 5.04; 5.12$	IIA
Germanium.....	Cubic	Diamond	Fig. 4	$a = 5.63; 5.61$	IIA
Tin (gray).....	Cubic	Diamond	Fig. 4	$a = 6.46$	IIA
Tin (white).....	Tetragonal	.....	.....	.....	IIIB
Lead.....	Cubic	Face-centred	Fig. 2	$a = 4.91$	IIA?
Vanadium.....	Cubic	Body-centred	Fig. 1	$a = 3.04$	IIA
Tantalum.....	Cubic	Body-centred	Fig. 1	$a = 3.272$	IIA
Antimony.....	Hexagonal	.....	.....	.....	IIIB
Bismuth.....	Hexagonal	.....	.....	.....	IIIB
Sulfur.....	Orthorhombic	.....	.....	.....	IIIB
Chromium.....	Cubic	Body-centred	Fig. 1	$a = 2.805$	IIA
Molybdenum.....	Cubic	Body-centred	Fig. 1	$a = 3.143; 3.08$	IIA
Tungsten.....	Cubic	Body-centred	Fig. 1	$a = 3.18; 3.150$	IIA
Alpha iron.....	Cubic	Body-centred	Fig. 1	$a = 2.86; 2.87$	IIA
Gamma iron.....	Cubic	Face-centred	Fig. 2	$a = 3.60 \text{ at } 1000^\circ$	IIA
Nickel.....	Cubic	Face-centred	Fig. 2	$a = 3.53; 3.54$	IIA
Cobalt.....	Cubic	Face-centred	Fig. 2	$a = 3.554$	IIA
Cobalt.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.514; c = 4.105$	IIA
Ruthenium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.686; c = 4.272$	IIA
Rhodium.....	Cubic	Face-centred	Fig. 2	$a = 3.820$	IIA
Palladium.....	Cubic	Face-centred	Fig. 2	$a = 3.950; 3.90$	IIA
Osmium.....	Hexagonal	Hex. close-packed	Fig. 3	$a = 2.714; c = 4.32$	IIA
Iridium.....	Cubic	Face-centred	Fig. 2	$a = 3.865$	IIA
Platinum.....	Cubic	Face-centred	Fig. 2	$a = 3.930; 4.02$	IIA



## INORGANIC COMPOUNDS NOT SALTS.

ALLOYS.—Most of the accumulated information concerning the structures of alloys is the result of two investigations using the powder method. In alloys<sup>43</sup> from pure nickel to 70 per cent. Fe – 30 per cent. Ni the structure is said to be face-centred cubic; beyond 70 per cent. Fe it is body-centred cubic. Similarly up to 80 per cent. of iron atoms<sup>43</sup> can be replaced by cobalt atoms before there is a shift from a body-centred cubic arrangement. With amounts of cobalt increasing beyond 80 per cent. the structure is said to pass through a mixture of face-centred and body-centred forms, pure face-centred and finally a mixture of face-centred cubic and hexagonal closest packed. The results of the study of copper-zinc alloys<sup>43</sup> are much more complicated, passing it is said through face-centred cubic (for copper), body-centred cubic, rhombohedral, and finally hexagonal arrangements (for zinc). In reporting this study<sup>43</sup> no numerical data of any sort (except compositions of alloys) are given, so that neither can the structures assigned be checked nor can any dimensional changes with composition be followed. In view of the probably correct simple structures of the metals themselves, it is likely that the nickel-iron and cobalt-iron alloys are correct, but when the complexity of the copper-zinc series is taken into account, it is impossible to lay great reliance upon these results as determinations of atomic arrangement. A 20 per cent. nickel-steel, which normally showed a practically pure face-centred cubic form, was made to develop strongly the body-centred modification after being chilled in liquid air.

Powder experiments<sup>41, 44</sup> upon nickel and manganese steels and upon other steels after various physical treatments have been described. It is concluded that in austenite the atoms have a face-centred arrangement, in martensite and in ordinary quickly drawn steel hardened at 1275° C. the atoms have the body-centred arrangement characteristic of  $\alpha$ -iron.

The following<sup>45</sup> has been published upon alloys of silver-palladium and of silver-gold: "An X-ray analysis of two graded series of alloys, extending from pure silver to pure palladium, and from pure silver to pure gold, shows that the edge of the unit cube in silver decreases progressively with the addition of palladium, but remains practically unchanged by the addition of gold. The effects of cold-work and of annealing have been observed.



Accurate values for the edges of the unit cubes, and corresponding densities of the pure metals and alloys have been obtained." \*

The investigation of the natural alloy of iridium and osmium, known as iridosmium,<sup>46</sup> furnishes what is from the standpoint of crystal structure determination by far the most satisfactory investigation yet made of any metal. Taking the diffraction data from Laue photographs and making use of the results of the theory of space-groups, it is shown that these data require the close-packed hexagonal arrangement of atoms. The parameter  $u$  defining the position of the second atom within the unit cell is taken as one-half, though the compelling reason for precisely this value is not clear. It is unfortunate that the specimen used in this study was of unknown chemical composition so that the dimensions resulting from it have little significance.

#### CARBIDES, ETC.

*Carborundum*, SiC.—The studies that have been made of the crystal structure of carborundum furnish another and striking example of the insufficiency of the older methods of investigation. Crystallographic information upon carborundum has given it hexagonal symmetry with an indication of trigonal characteristics. Recently evidence<sup>47</sup> of a purely crystallographic sort has been adduced which points to the existence of three distinct types of crystals. Laue photographs<sup>48</sup> have subsequently been made from crystals of these three supposed kinds. Two of the modifications appear to be truly hexagonal, the third is surely trigonal. The relations supposed to exist between these forms are unusual for independent modifications of a substance.

Three investigations have been made of the structure of carborundum: One<sup>49</sup> by the original spectrometer technic, one with powder data<sup>50</sup> (neither of these has made any use of the results of the theory of space-groups) and one<sup>51</sup> that makes use of Laue photographic and spectrographic data and of space-group results. From the spectrometric data a structure was deduced<sup>49</sup> which was like that of the diamond if half of the carbon atoms are replaced by silicon atoms and if the silicon atoms as a whole are considerably displaced along trigonal axes. A Laue photo-

---

\* A detailed account of these experiments has recently appeared.<sup>131</sup> The following dimensions for gold, silver and palladium are included:  $a = 4.075\text{A.U.}$ ;  $a = 4.080\text{A.U.}$ ;  $a = 3.900\text{A.U.}$



graph, published by one of these authors in a different place,<sup>52</sup> shows a hexagonal symmetry which (if it is due to an untwinned specimen) is not in agreement with the assigned structure. Calculations<sup>53</sup> based solely upon electromagnetic theory (the details of which are not given) have been thought to make the spectrometer results agree with an undistorted diamond arrangement. Later powder data<sup>50</sup> are said to give the lines of both the cubic and hexagonal close packing; this is considered to show that crystals of carborundum are a combination of both of these arrangements. Only in face of information of the most convincing character would one be justified in seriously considering the reality of such a hybrid as this; as yet no data of any sort have appeared. The third investigation,<sup>51</sup> which made use principally of Laue photographic data, was carried out with a full awareness of the crystallography of carborundum. A structure for the second type has been obtained which contains twenty-four chemical molecules within the unit cell. It is stated that the other two forms likewise have units of the same absolute size and contain twenty-four molecules. From the discussion which accompanies this study of structure, it is not clear that so large a unit cell must be chosen, and it does not seem permissible to make a definite decision concerning the structure of carborundum until the investigations have been made more complete. In the meantime it is apparent that the unaided spectrometric and powder photographic data have proved themselves totally inadequate for handling this crystal.

#### OXIDES.

MONOXIDES OF UNIVALENT ELEMENTS.—Diffraction data have been collected from three of these oxides: Silver oxide, cuprous oxide and ice. For the first of these only powder data are at hand, for the second both powder and rough spectrometric measurements, while for ice diffraction data by all methods have been published.

*Ice, H<sub>2</sub>O.*—A Laue photograph<sup>54</sup> has been prepared which is said to assign ice to the hexagonal division of the hexagonal system with an axial ratio of  $c:a = 1.678$ . Proceeding upon the assumption that such a Laue photograph really was obtained from a single crystal and not from a twinned trigonal form, a theoretically well-developed study<sup>55</sup> has been given of the atomic arrangement. Two molecules are found associated with a unit of the



dimensions:  $a = 3.46\text{A.U.}$ ,  $c = 5.53\text{A.U.}$ . The data are not sufficient to place the atoms accurately within this unit. According to spectrometric results<sup>56</sup> the hexagonal unit has a length  $a = 4.74\text{A.U.}$  and a height  $c = 6.65\text{A.U.}$ , corresponding to the axial ratio  $c:a = 1.4026$ . Four molecules are contained within this unit cell, the coördinate positions (presumably of the oxygen atoms) being given as  $000$ ;  $1/3, 2/3, 1/z$ ;  $1/3, 2/3, 1/2$ ;  $0, 0, (z+2)/2z$ , where the value of  $z$  is indeterminate. The powder photographic data,<sup>57</sup> on the other hand, have been interpreted to yield a unit of yet another size:  $a = 4.52\text{A.U.}$ ,  $c = 7.32\text{A.U.}$ ; axial ratio,  $c:a = 1.62$ . Though these axial ratios are appropriately related to one another, one as the result of a rotation through  $30^\circ$  with respect to the other, the absolute dimensions of the unit cells in the last two instances are not similarly related. The close approximation of the axial ratio taken from powder data to that of the closest packed grouping of spheres ( $c:a = 1.633$ ) is taken as an indication that the molecules of water are associated into  $\text{H}_4\text{O}_2$  groups which are themselves closely packed. As an unconscious illustration of the ease with which different structures can be assigned to a crystal by this older procedure, a still different interpretation<sup>58</sup> has been given to these same data.

Of the various studies upon ice only one<sup>55</sup> has any worth as a determination of the atomic arrangement. On the other hand, the best experimental data are powder measurements.<sup>57</sup> In view of the disagreement between these investigations in the determination of the size and shape of the correct unit cell, and because the data open to the least question do not accompany the best study of structure, it is not permissible to decide which, if any, of these studies may be correct.

*Cuprite*,  $\text{Cu}_2\text{O}$ .—Spectrometric data<sup>59</sup> have been obtained from crystals of cuprite, but have not been reported except in a rough graphical form. They appear to agree with a unit cube which contains two chemical molecules and has the length of side:  $a = 4.32\text{A.U.}$  The coördinate positions within this unit cube (Fig. 5) are:

Copper:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ .  
Oxygen:  $000$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

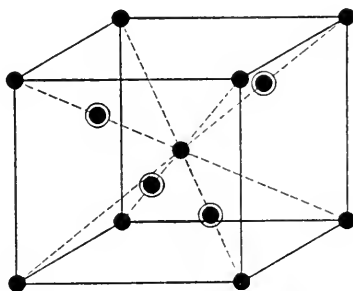
Powder photographic data,<sup>60</sup> concerning which nothing has been published, are said to yield  $a = 4.26\text{A.U.}$  Very recently<sup>61</sup> an



adequate treatment of powder photographic data leads to the same structure, also with  $a = 4.26\text{A.U.}$

*Silver Oxide,  $\text{Ag}_2\text{O}$ .*—A study<sup>62</sup> of the structure of this substance has been carried out with use of the results of the theory of space-groups, the data being taken from powder photographs. It is shown that the cuprite arrangement (Fig. 5) given above is the only possible structure if the unit cube is a simple one containing two, and not sixteen, chemical molecules. Furthermore, no lines were found upon the photographs which were not in agreement with this smaller unit. The length of its side was

FIG. 5.



The unit cube of the "cuprite arrangement." In the compound  $\text{R}_2\text{X}$ , the atoms of X are indicated in this figure by the solid circles.

found to be  $a = 4.77\text{A.U.}$  Another study<sup>60</sup> of silver oxide, data upon which have never been published, gives a unit cell of length  $4.69\text{A.U.}$  This structure has recently been confirmed<sup>61</sup> by another treatment of powder data which yields a dimension lying between the other two:  $a = 4.718\text{A.U.}$

**MONOXIDES OF THE DIVALENT METALS.**—Except for magnesium oxide and zinc oxide only powder photographic data have been collected. Aside from beryllium oxide and zinc oxide which have a hexagonal symmetry, and cupric oxide which is triclinic, all have been given a "sodium chloride arrangement" (Fig. 6). The detailed treatment of the case of magnesium oxide\* has shown that this latter structure is the only one which may properly be deduced from the existing experimental data. It seems quite certain, though the published data are in many cases scarcely convincing, that the other cubic oxides have this same structure. Zinc oxide has received a thorough treatment with data from Laue and powder photographic and spectrometric sources and

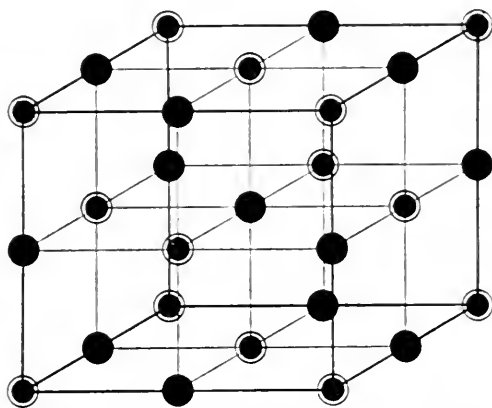
\* See also the analogous treatment of sodium chloride by P. Niggli, "Geometrische Krystallographie des Discontinuums," p. 435, etc., Leipzig, 1919.



from the general similarity of their powder data it is probable that beryllium oxide has the same type of structure. A lengthy discussion of powder photographic data is believed to give a distorted "sodium chloride arrangement" of the atoms in cupric oxide.

*Cupric Oxide, CuO.*—Taking the data from powder photographs, a structure has been deduced<sup>61</sup> for this triclinic crystal which conforms with the crystallographic data.<sup>61, 70</sup> Though this arrangement, which is a distortion of that of sodium chloride (Fig. 6), does not appear to be uniquely determined, it is probably

FIG. 6.



The unit cube of the "sodium chloride arrangement." In the compound  $RX$  either the atoms of  $R$  or those of  $X$  may be represented by the solid circles.

correct. For a detailed description reference must be made to the original article.

*Beryllium Oxide, BeO.*—Two studies have been made of powder photographic data from beryllium oxide. As a result of one of them<sup>63</sup> it was given the "sodium chloride arrangement," but in view of its well-known hexagonal symmetry little significance can be attached to this work. The experimental results of the other investigation<sup>10</sup> are said to correspond to a unit hexagonal cell of length of side  $a = 2.696 \text{ A.U.}$  and height  $c = 4.394 \text{ A.U.}$ , and to be at least consistent with the "zinc oxide structure" (Fig. 7) to be described below.

*Magnesium Oxide, MgO.*—Besides the powder photographic data,<sup>65, 66, 63, 67, 26, 69, 70</sup> which have been collected by various observers, Laue photographs were studied in connection with the application of the results of the theory of space-groups.<sup>68</sup> The structure is that of the "sodium chloride arrangement" (Fig. 6).



in which the atoms have the following coördinate positions within the unit cube:

Magnesium:	000; $0\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}0$ ; $\frac{1}{2}0\frac{1}{2}$ .
Oxygen:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}00$ ; $00\frac{1}{2}$ ; $0\frac{1}{2}0$ .

Various determinations of the length of the side of the unit cube have been published:  $4.22 \pm 0.02$  A.U.; 4.19 A.U.; 4.20 A.U.; 4.18 A.U.; and 4.22 A.U. From these values the most probable one appears to be 4.20 A.U.

*Calcium Oxide*, CaO.—Of the reported studies,<sup>26, 63, 66</sup> one<sup>63</sup> contains data in substantiation of the “sodium chloride structure” (Fig. 6). The length of the side of the unit cube is variously stated as: 4.74 A.U.;  $4.77 \pm 0.05$  A.U.; 4.84 A.U.

*Strontium Oxide*, SrO.—The single published determination<sup>26, 63</sup> of strontium oxide gives the length of the edge of the unit cube:  $a = 5.104 \pm 0.01$  A.U.

*Barium Oxide*, BaO.—The two determinations<sup>26, 63</sup> of the side of the unit cube give:  $a = 5.47$  A.U. and  $5.50 \pm 0.02$  A.U.

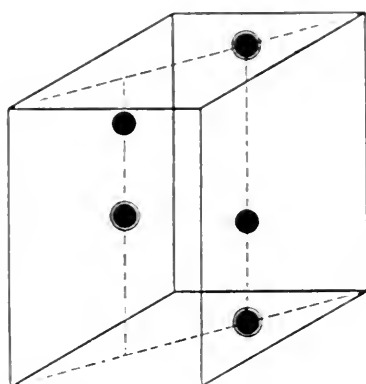
*Zinc Oxide*, ZnO.—Diffraction data have been collected by all three of the methods now available. An assignment of structure was made upon the basis of the first (spectrometric) measurements.<sup>34, 72</sup> It appears early to have been indicated<sup>73</sup> (the original papers are not available), and since has been shown,<sup>74</sup> that these spectrometric data do not satisfactorily establish the assigned structure as the only possible one. In the endeavor to distinguish between the different structures that remain possibilities in the light of the spectrometer measurements, Laue<sup>74</sup> and powder<sup>70</sup> photographs<sup>75</sup> have been examined with the help of the results of the theory of space-groups. This latter investigation is one of the best that have been made of any crystal. It is shown that neither the spectrometric observations nor the Laue photographic data are able to decide conclusively between the two arrangements listed below though they favor somewhat the particular arrangement (see I below), which the spectrometer results were supposed to have established. The powder data likewise are in somewhat better agreement with arrangement I. The length of the side of the unit hexagonal prism containing two molecules is determined as:  $a = 3.22$  A.U., its height  $c = 5.18$  A.U., corresponding to the axial ratio  $c : a = 1.608$ . The two arrangements that remain possibilities have the following coördinate positions:



- Possibility I: Zinc:  $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$  ( $u$  is here taken as 0)  
 Oxygen:  $\frac{1}{3}, \frac{2}{3}, u; \frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}$ .  
 Possibility II: Zinc:  $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ . ( $u$  is here taken as 0)  
 Oxygen:  $00u; 0, 0, u + \frac{1}{2}$ .

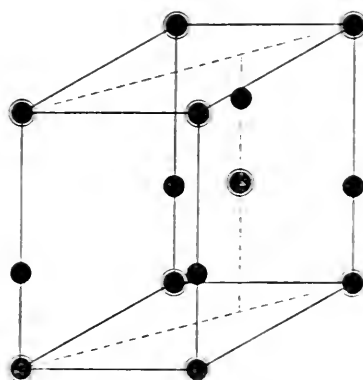
For both arrangements the data are best fitted by a value of  $u$  around  $5/8$ , but the experiments are not able to place it with accuracy. The unit cell of I, which is to be taken as the prob-

FIG. 7a.



The hexagonal unit of the "zinc oxide arrangement." The positions of the oxygen atoms within the unit are indicated by the black circles.

FIG. 7b.



This is the same atomic arrangement as 7a with the origin of coördinates shifted to the point  $(\frac{1}{3}, \frac{2}{3}, 0)$  of the previous figure.

ably correct arrangement, is shown in Fig. 7a, while the unit cell of Fig. 7b is the same distribution with the origin shifted to the point  $(\frac{1}{3}, \frac{2}{3}, 0)$  of the first set of coördinates in order to make it agree in appearance with that previously shown.

This is an excellent example of the insufficiency of methods of crystal structure study which do not make use of the theory of space-groups.

*Cadmium Oxide, CdO.*—Two determinations<sup>66, 76</sup> of the structure of cadmium oxide, both with powder photographs, give



it the "sodium chloride arrangement" (Fig. 6). The length of the edge of the unit cube is stated as 4.72A.U. Data are given for only one <sup>76</sup> determination.

*Nickel Oxide*, NiO.—Statements <sup>66, 71</sup> of the structure of nickel oxide as that of the "sodium chloride arrangement" place the length of the side of the unit cell as 4.20A.U. and 4.14A.U. In neither case have any data been furnished. Unanalyzed powder data <sup>70</sup> also have been published.

*Cobalt Oxide*, CoO.—Powder photographic data which have been published <sup>70</sup> without their having been worked over for the determination of structure are said to agree with the "sodium chloride arrangement."

DIOXIDES.—Attempts have been made to determine the structures of the following dioxides: SiO<sub>2</sub> as quartz; TiO<sub>2</sub> as rutile and as anatase; ZrSiO<sub>4</sub> as zircon; SnO<sub>2</sub> as cassiterite and ThSiO<sub>4</sub> as thorite. Quartz has trigonal symmetry, the rest are tetragonal, and any discussion which does not treat in detail the many arrangements which become possible in the light of this lower symmetry can have little claim to definiteness. For this reason alone the structures of none of these crystals can be considered as determined even with some degree of probability.

*Quartz*, SiO<sub>2</sub>.—On the basis of some spectrometric observations <sup>35</sup> an atomic arrangement for quartz has been proposed which is built upon a hexagonal unit of structure. From the same data an arrangement has been presented <sup>77</sup> which places the silicon atoms upon a rhombohedral lattice. As determinations of the structure of quartz, either one of these discussions is so totally inadequate that there is no justification for detailed treatment. Much more work, both in the collection of data and in their interpretation, must be carried out before we will have any real indication of the manner of arrangement of the atoms in quartz.

*Rutile*, TiO<sub>2</sub>.—Only spectrometric data are available for the determination of the atomic arrangement in either rutile or anatase. Two investigations have been made upon rutile which do not agree in the data <sup>9, 79</sup> found and which consequently assign to it different structures. The later <sup>79</sup> of the studies gives it a structure which is almost unbelievably complicated. Not only the experimental information but the treatment to which these data have been subjected are incapable of establishing the correct structure for this crystal.



*Anatase*,  $\text{TiO}_2$ .—One investigation<sup>80</sup> has been made upon crystals of anatase in which also the data and treatment are incapable of establishing its structure.

*Zircon*,  $\text{ZrSiO}_4$ .—The studies<sup>9</sup> upon zircon are of the same character and apparently of the same value as those upon anatase.

*Cassiterite*,  $\text{SnO}_2$ .—The investigations<sup>9, 79</sup> on cassiterite parallel those upon rutile, though somewhat more fragmentary. Powder data<sup>70</sup> have been published but with no attempt to establish its structure.

*Thorite*,  $\text{ThSiO}_4$ .—Thorite<sup>9</sup> is commonly found in an altered condition and it is therefore not surprising that the specimens studied could not be made to furnish spectrometric reflections.

TRIOXIDES.—Reflections<sup>81</sup> have been made from a few faces of hematite ( $\text{Fe}_2\text{O}_3$ ) and of ruby ( $\text{Al}_2\text{O}_3$ ). On the basis of these measurements they have been assigned a structure which resembles that of calcite. The data and the determinations based upon them are not, however, in any sense sufficient for establishing this arrangement and its discussion is not justified. Measurements of dimensions of a unit cell based upon powder photographs have been recorded though no data accompany this statement. Unanalyzed powder data<sup>70</sup> also have appeared.

#### HYDROXIDES.

Manganese and magnesium hydroxides are the only members of this group whose structures have been studied. They occur as the trigonal minerals, pyrochroite and brucite. Laue photographs have been prepared and their structures deduced with some use of the results of the theory of space-groups. Powder data have also been prepared from precipitated  $\text{Mg}(\text{OH})_2$  and have been shown to agree with the atomic arrangement for brucite.

*Pyrochroite*,  $\text{Mn}(\text{OH})_2$ .—This structure<sup>82</sup> was deduced entirely from Laue photographic data. The unit cell developed from the lattice  $\Gamma_h$  contains one chemical molecule and is calculated to have the dimensions:  $a = 3.34\text{A.U.}$ ,  $c = 4.68\text{A.U.}$  ( $c : a = 1.40$ ). The arrangement of the atoms within this unit cell (Fig. 8) is expressed by the coördinates:

Manganese:	000.
Oxygen:	$\frac{1}{3}, \frac{2}{3}, u$ ; $\frac{2}{3}, \frac{1}{3}, \bar{u}$ .
Hydrogen:	$\frac{1}{3}, \frac{2}{3}, v$ ; $\frac{2}{3}, \frac{1}{3}, \bar{v}$ .

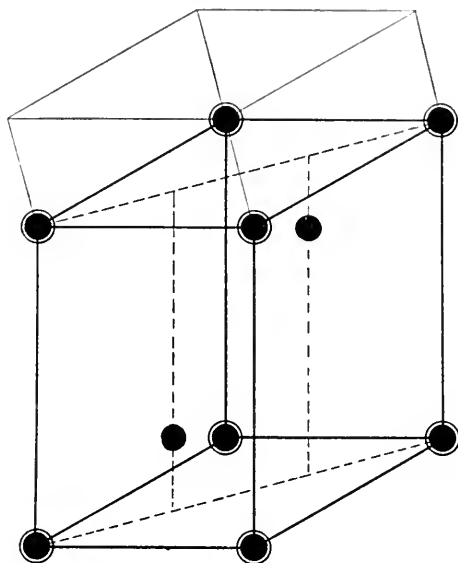
From a consideration of Laue photographic data it is shown that



$u$  cannot have a value greater than 0.833 nor less than 0.75. The best fit was found for a value of  $u = 7/9 = 0.778$  if the usual scattering assumptions are made. The parameter  $v$  (for hydrogen) is indeterminable.

*Brucite*,  $\text{Mg}(\text{OH})_2$ .—In the arrangement of its atoms brucite<sup>82</sup> is strictly isomorphous with  $\text{Mn}(\text{OH})_2$ ; the axial ratio is, however,  $c:a = 1.5208$ . The calculated dimensions of the unit (Fig. 8) containing a single molecule thus become:  $a = 3.13\text{-A.U.}$  and  $c = 4.75\text{A.U.}$  It is considered that the parameter for

FIG. 8.



The hexagonal unit cell of the "pyrochroite,  $\text{Mn}(\text{OH})_2$ , arrangement." The oxygen atoms are indicated by black circles; the hydrogen atoms are not shown because the positions are indeterminable but they must lie somewhere upon the same vertical lines of the figure as the oxygen atoms. In cadmium iodide iodine atoms are represented by the black circles.

oxygen has the same value as in pyrochroite. Powder photographic data<sup>83</sup> from precipitated  $\text{Mg}(\text{OH})_2$  are in agreement with this structure, but they are incapable of furnishing satisfactory data for even approximately placing the oxygen atoms.

(To be continued.)



# THE INFLUENCE OF STIRRING ON THE RATE AND COURSE OF DEVELOPMENT.\*

BY

S. E. SHEPPARD and FELIX A. ELLIOTT.

Research Laboratory, Eastman Kodak Company.

THE importance of stirring on development as influencing uniformity has been the subject of frequent comment and not a few definite investigations. Some of the more noteworthy of these are referred to below.<sup>1</sup> In most cases the object of these has been simply to reduce lack of uniformity to a minimum, by suitable mechanical and other precautions, without much inquiry as to what phases of the process allowed such an influence. The work described in the following was undertaken as part of a general investigation of the dynamics of development, and with the particular purposes of ascertaining:

1. Dependence of the mechanical factors on nature of the developing agent;
2. How the mechanical factors may affect uniformity.

## EXPERIMENTAL.

In the investigations of Sheppard and Mees<sup>2</sup> on the development dynamics, using plate slips, the slips placed back to back, were rotated in pairs vertically in tubes containing the developer. While this method has been found fairly satisfactory in a large body of sensitometric and kindred investigations, our own examination has shown that the method was not free from error in the matter of uniformity, and that this again was sensitive to the rate of stirring. Recently<sup>3</sup> a very detailed investigation has been made by T. Otashiro of the deviations from uniformity of development with this mode of operation, but using a much

---

\* Communicated by Dr. C. E. K. Mees, Director of Laboratory and Associate Editor of this JOURNAL. Published as Communication No. 157 from the Research Laboratory of the Eastman Kodak Company

<sup>1</sup> A. Caillier: *Phot. J.*, **53**, 242 (1913); F. F. Renwick, *ibid.*, **52**, 254 (1912); O. Bloch, *ibid.*, **61**, 425 (1921).

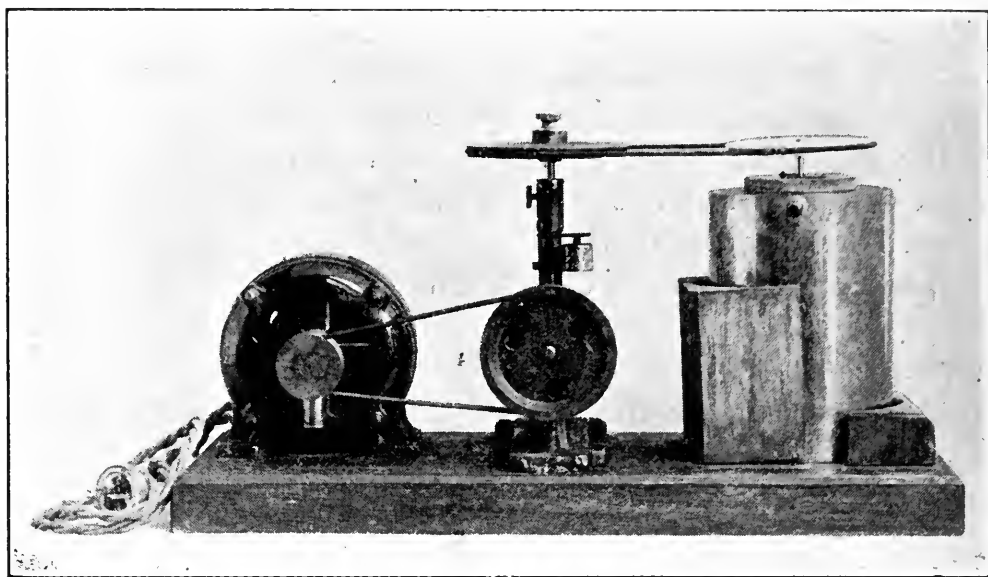
<sup>2</sup> "Investigations on the Theory of the Photographic Process," 1907 (Longmans, Green and Co.).

<sup>3</sup> *Bull. Kirya Tech. College (Japan)*, May, 1921.



larger plateholder (*viz.*, about 13 cms. wide by 21 cms.)<sup>4</sup> From this it is concluded that "when a dry plate is developed in such a way that it is at first immersed in water, with or without rotation about a vertical axis, and then rotated about the axis in the ferrous oxalate developer, there is a regular difference of the photographic density between the upper and the lower portion, and also between the left-hand side and the right-hand side of the

FIG. 1a.



Developing apparatus.

plate, according to the property of the developer and the rotation of the plate in the liquid, though it is uniformly exposed."

Although the conditions in Otashiro's investigation, due to the greater size of the plate, exaggerated the defective uniformity of the vertical rotation method, it is evident that this must exist on a smaller scale. His further conclusion, in favor of vertical development at rest, is satisfactory in this regard, provided no great contrasts of density exist in the plate. Otherwise, as shown by E. R. Bullock<sup>5</sup> the convection currents produced under these conditions are likely to cause trouble.

For the majority of the work on the development process in hand in this Laboratory the use of portrait film has been pre-

<sup>4</sup> Cabinet size.

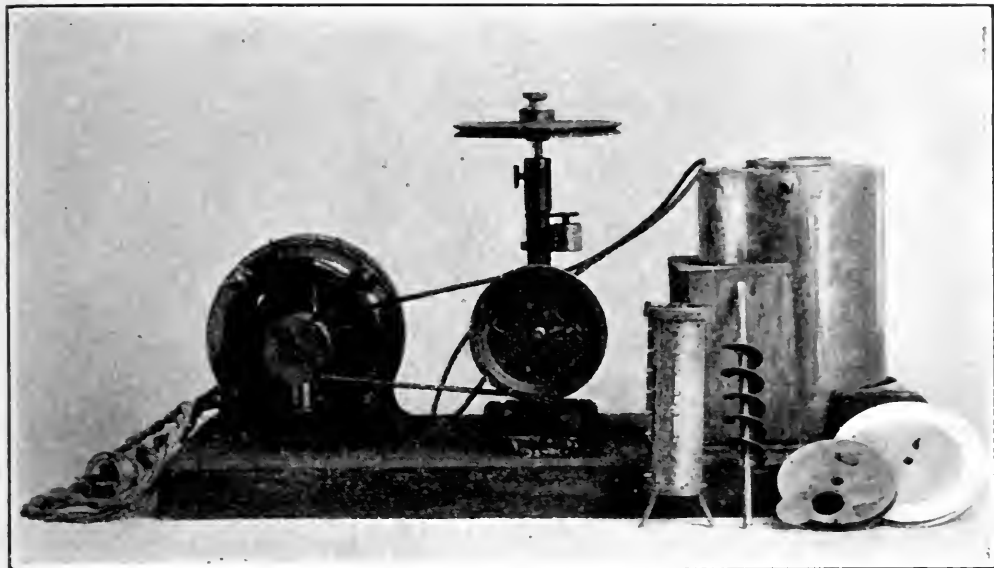
<sup>5</sup> *B. J.*, 69, 110 (1922).



ferred, as giving the most uniform material, particularly in respect to coating. The flexibility of the film support lent itself to the construction of a drum type of developing vessel, in which:

1. Several sensitometric strips  $3\frac{1}{4}'' \times 1''$  could be developed simultaneously.
2. The rate of stirring could be varied over a considerable range.

FIG. 1b.



Developing apparatus: assembly.

3. Uniform stirring of the liquid relative to the developing surface could be secured at practically all speeds of stirring.

This apparatus enabled us, therefore, to investigate for itself the mechanical factor in development as primarily *velocity of flow of developing solution* over the gelatin surface, largely uncomplicated by secondary effects of the velocity-potential of the flow, such as eddies, accelerations and decelerations, inequalities of velocity, etc.

The apparatus, a photograph of which is shown in Figs. 1a and 1b and a diagram in Fig. 2, consists essentially of a removable central draft-tube, forming the drum on which the film slips are wound preparatory to development. This drum fits down in the cylindrical developing tube or vessel; the screw agitator is placed inside the draft tube, then developer poured in, the cover and



pulley slipped on, and rotation started. This procedure was found on the whole to give the least initial delay, about five seconds elapsing between immersion in the developer and the commencement of rotation.

The developing chamber, as will be seen from the photograph,

FIG. 2.

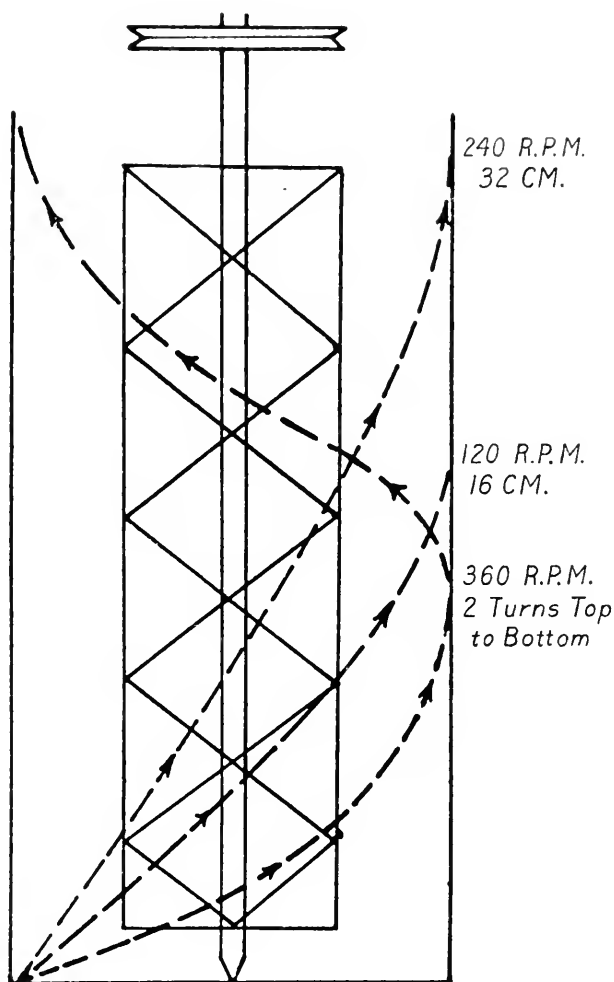


Diagram of developing apparatus showing circulation at different speeds.

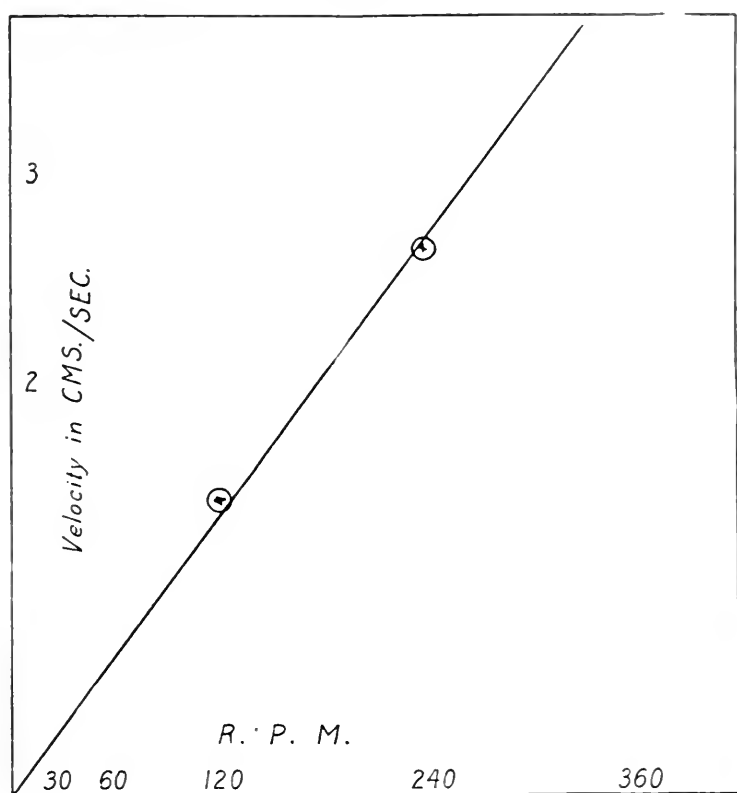
is jacketed, and water at constant temperature is circulated through the jacket from a thermostat.

*Character of the Motion.*—The relation between the stirring velocity and the motion was analyzed as follows: A special counter on the shaft of the agitator enabled the r.p.m. to be determined. The apparatus was assembled with a glass container of



the same dimensions in place of the regular metal developing vessel, and the speed of motion of the fluid observed by following the movement of small pieces of cotton, and by the rate of distribution of drops of dye solution admitted when definite rates of rotation had been installed. The values were as follows:

FIG. 3.

*Velocity of Cotton Particles.*

R.P.M.	Time.	Distance.	Velocity cms. per sec.
120	11.5 secs.	15 cms.	1.3
240	5 secs.	14 cms.	2.8
	14 secs.	32 cms.	2.3
360	14 secs.	56 cms.	4.0

} 2.6

These results show that the velocity is sensibly proportional to the r.p.m. (see Fig. 3) and give figures for the rate at which the solution is renewed at the surface of the film. At the same time, the path of a particle of the liquid alters its character, in the sense that it travels over a helix of lower pitch and greater frequency as the r.p.m. increase. (See Fig. 2.)

To test the question of general equalization, drops of concen-



trated dye solution were inserted and the time for uniform distribution observed.

*Velocity of Attaining Uniform Concentration.*

R.P.M.	Time of Equalization.	Relative Velocity.
496	6. secs.	.167
260	10.5 secs.	.095
174	16.0 secs.	.062

These results again showed that the velocity was proportional to the r.p.m. At the same time, they give some idea of the time required, at a given r.p.m., to reduce the excess concentration of a soluble reaction component at the surface of the emulsion to uniform distribution throughout the volume of solution used. These results show that improvement in the mechanism is possible, and to secure this a planetary gearing is being introduced by which the drum carrying the film instead of being stationary is rotated in the opposite sense to the screw. The results reported in this paper were obtained with the simpler type.

The film strips were exposed in a Jones non-intermittent sensitometer <sup>6</sup> fixed in acid hypo, washed, dried at constant humidity, and the densities measured with a Martens photometer. Densities including fog were plotted as functions of  $\log E$ , in the usual manner for constructing the characteristic curves. From occasions of space, it is not possible to reproduce tables and curves of the complete data; the methods developed by A. H. Nietz <sup>7</sup> of determining the convergence point in case of retarded development, and the gamma-time curve were employed. We give as exemplary the following characteristic curves for the course of development at different velocities of stirring for a *hydroquinone: sodium carbonate* developer, which showed the greatest anomaly of those developers examined. (See Figs. 4, 5 and 6.)

It will be seen from these that the principal change with increased stirring velocity is not a change in *gamma* (see later) but a shift in the position of the convergence point of the straight line portions of the  $D$ ,  $\log E$  curves. This corresponds to the

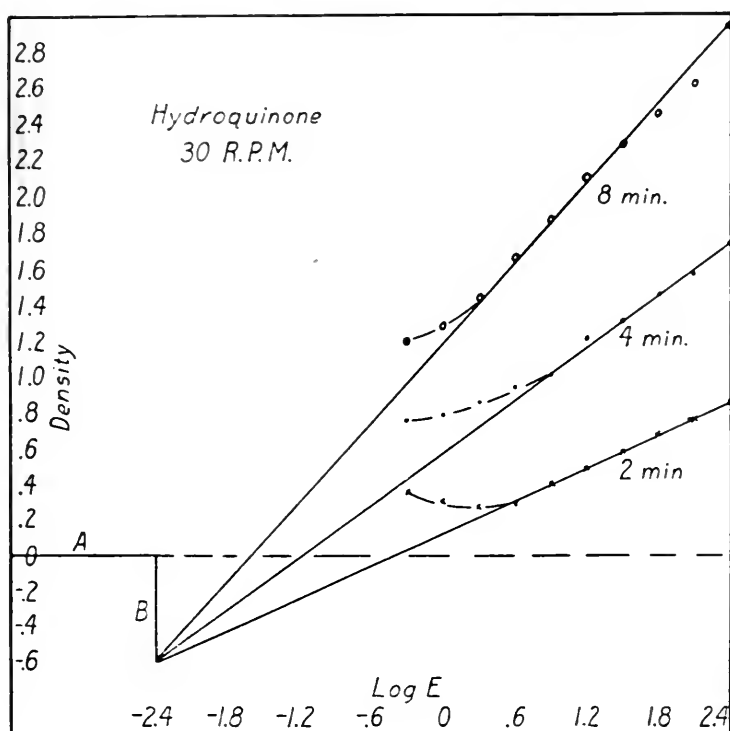
<sup>6</sup> *Phot. J.*, 40, 80 (1920).

<sup>7</sup> *Phot. J.*, 60, 280 (1920). A more complete account in press as Monograph 3 on Theory of Photography from the Research Laboratory of the Eastman Kodak Company.



behavior of plates in a developer to which bromide has been added, or containing bromide, or, generally, to what has been termed "retarded development."<sup>s</sup>

FIG. 4.



In the case considered development for different times is yielding a family of straight lines meeting in a point, the coördinates of which are :

$a$ —abscissa in  $\log E$  units;

$b$ —ordinates in density units,

so that the equation of the curve is

$$D = \gamma(\log E - a) + b$$

which becomes identical with the normal equation  $D = \gamma (\log E - \log i)$  when  $b = 0$ . The criterion for the intersection of the straight lines is that  $D$  is a linear function of  $\gamma$ , i.e.,

$$D = \theta(\gamma - a).$$

Examining the action of bromide, Nietz found that  $a$  is independent of the bromide concentration,  $b$  increases negatively as the bromide concentration is increased.

<sup>s</sup> S. E. Sheppard: *J. Chem. Soc.*, 89, I, 530 (1906).



FIG. 5.

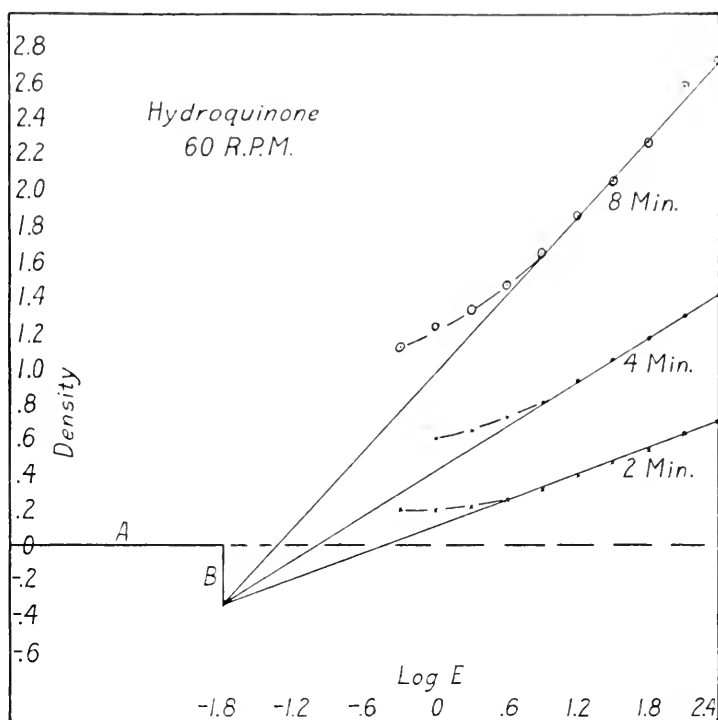
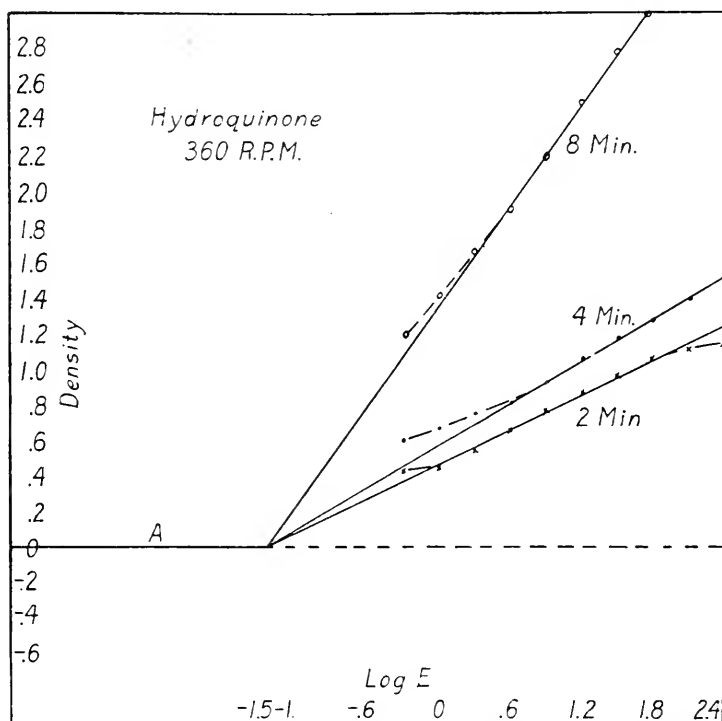


FIG. 6.





The values of  $a$  and  $b$  for the developers used were tabulated for different velocities, as also the values of  $\gamma_t$  the development coefficient for time  $t$ .

FIG. 7.

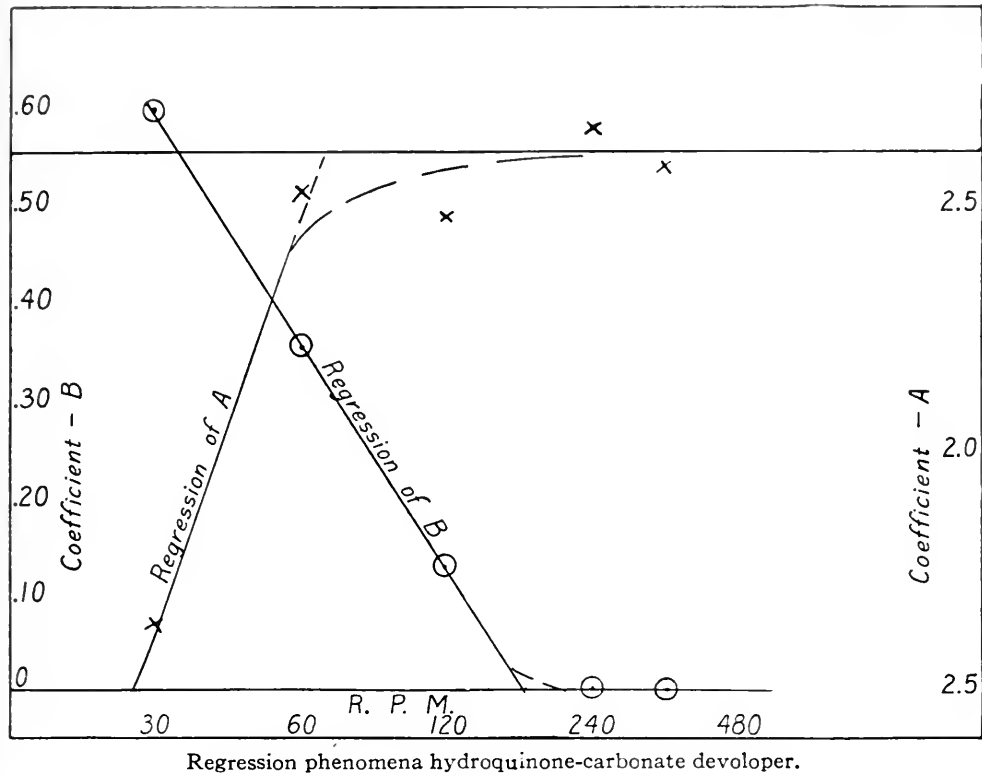


TABLE I.

Developer		5.5 gms. = $\frac{1}{20}$ molar		
Hydroquinone		50 gms.		
Na <sub>2</sub> SO <sub>3</sub>		59 gms.		
Na <sub>2</sub> CO <sub>3</sub>		1000 c.c.		
With water to		Velocity		
R.P.M.			$a$	$b$
Series i	30	.32	-2.40	0.60
	ii		-2.35	0.70
	iii		-2.35	0.51
Series i	60	.65	-1.32	0.40
	ii		-1.32	0.30
	iii		-1.80	0.36
Series i	120	1.3	-1.71	0.15
	ii		-1.35	0.10
Series i	240	2.6	-1.35	0.00
	ii		-1.35	0.00
	iii		-1.35	0.00
Series i	360	4.0	-1.46	0.00
	ii		-1.41	0.00



We have plotted these values of  $a$  and  $b$  as functions of the logarithms of r.p.m., *i.e.*, of velocities of stirring. It will be seen from the table and the curves (Fig. 7), that while there is some shift in the absolute value of  $a$  it soon attains a constant value, while  $b$  steadily diminishes with increasing stirring velocity, and becomes negligible at 240 r.p.m. This means that while hydroquinone with sodium carbonate is liable to behave as a retarded developer (without addition of bromide) under ordinary conditions of development, this retardation is overcome by increasing the velocity of stirring, so that it tends to behave normally. It is obvious that at the same time the Watkins factor will be increased somewhat. The relation of  $\gamma t$  to the r.p.m. is shown in the following table and figure (see Fig. 8) :

TABLE II.  
Hydroquinone-carbonate.

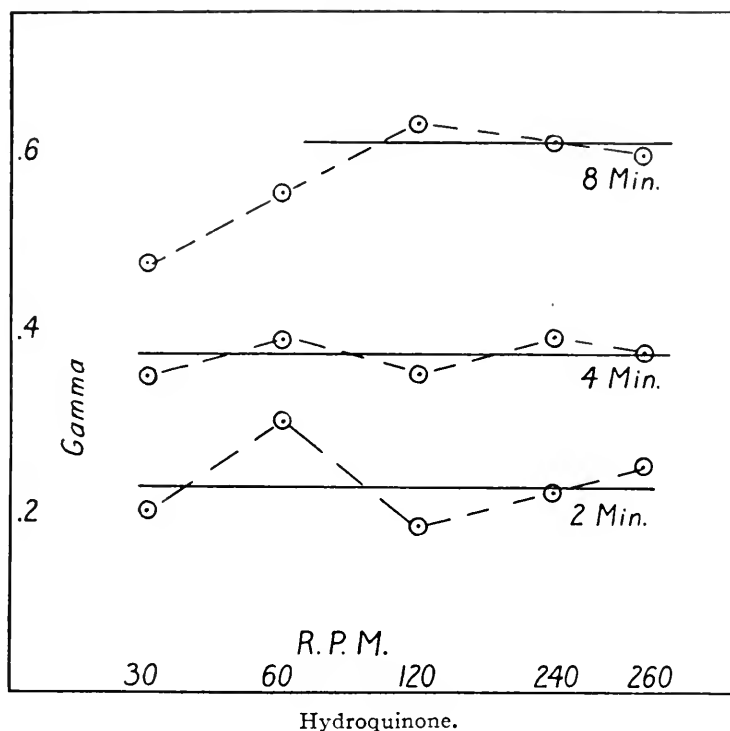
R.P.M.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.
30	.204	.324	.480
	.155	.255	.382
	.154	.480	.532
	.300		
Average	.200	.353	.465
60	.353	.280	.487
	.380	.437	.486
	.310	.435	.690
Average	.304	.384	.554
120	.211	.340	.582
	.145	.395	.700
			.610
Average	.180	.368	.630
240	.160	.453	.600
	.295	.405	.680
	.206	.320	.580
Average	.220	.393	.620
360	.279	.500	.596
	.214	.270	.582
Average	.246	.385	.589

It will be seen that up to four minutes there is no definite variation of  $\gamma$  with rate of stirring; at six minutes there is indi-



cation of some increase of  $\gamma$  up to 120 r.p.m., after which it remains independent of the velocity. Before considering any explanation of these results, we will give the data for other developers examined.

FIG. 8.

TABLE III.  
Pyrogallol.

Standard Formula

Pyrogallol	6.3 gms. = 1/20 molar
Na <sub>2</sub> SO <sub>3</sub>	50 gms.
Na <sub>2</sub> CO <sub>3</sub>	50 gms.
Water to	1000 c.c.

R.P.M.	Velocity.	<i>a</i>	<i>b</i>
30	.32	-1.30	0.10
60	.65	-1.30	0.00
120	1.30	-1.30	0.00
240	2.60	-1.30	0.00
360	4.00	-1.30	0.00

R.P.M.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.	$\gamma$ 16 mins.	$\gamma$ 32 mins.
30	.225	.355	.515	.720	1.060
60	.202	.338	.532	.800	1.100
120	.226	.350	.525	.770	1.075
240	.265	.425	.612	.825	1.078
360	.267	.475	.738	.955	1.113



FIG. 9.

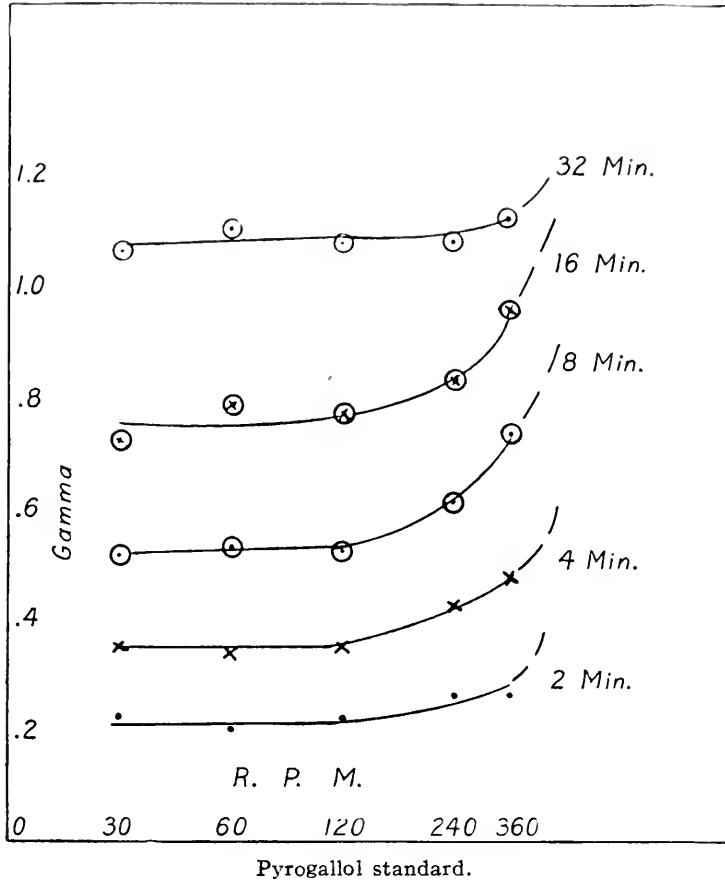
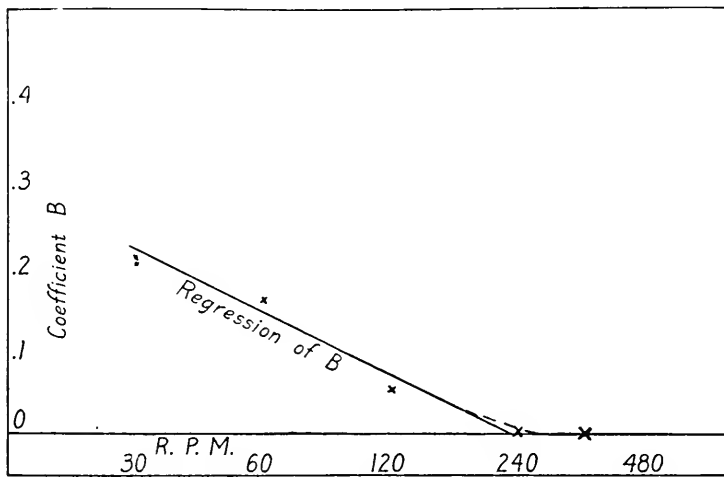


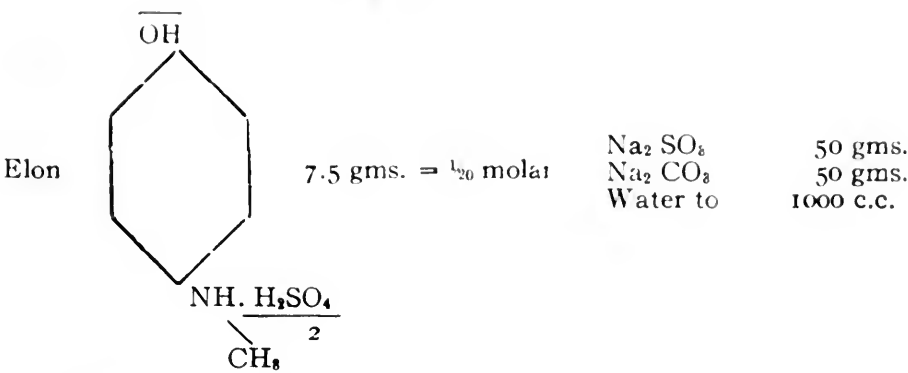
FIG. 10.



Elon.  
Regression effect in *elon* developer.



TABLE IV.  
Elon



R.P.M.	Velocity.		a	b
30	.32		-1.23	.29
60	.65		-1.27	.37
120	1.30		-1.23	.10
240	2.60		-1.20	.06
360	4.00		-1.20	.10

R.P.M.	$\gamma$ 1 min.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.
30	.340	.460	.600	.650
60	.365	.475	.590	.660
120	.330	.470	.592	.630
240	.368	.500	.590	.670
360	.410	.500	.680	.710

FIG. 11.

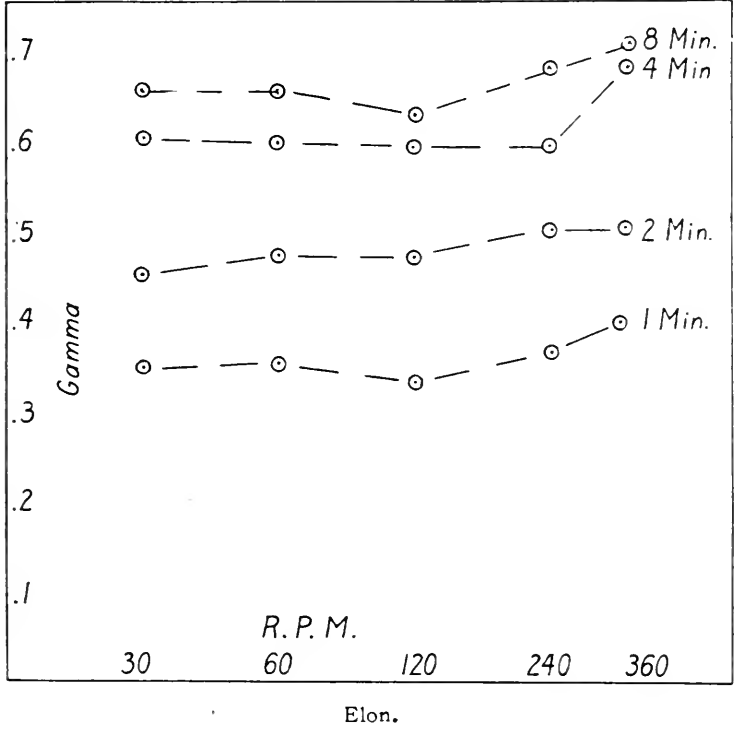
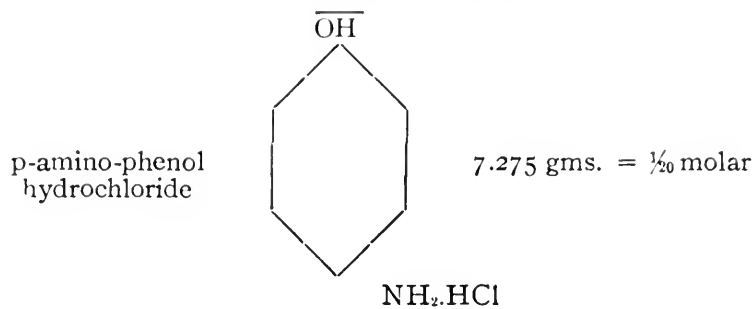




TABLE V.

Experiment 224.

P-amino-phenol.

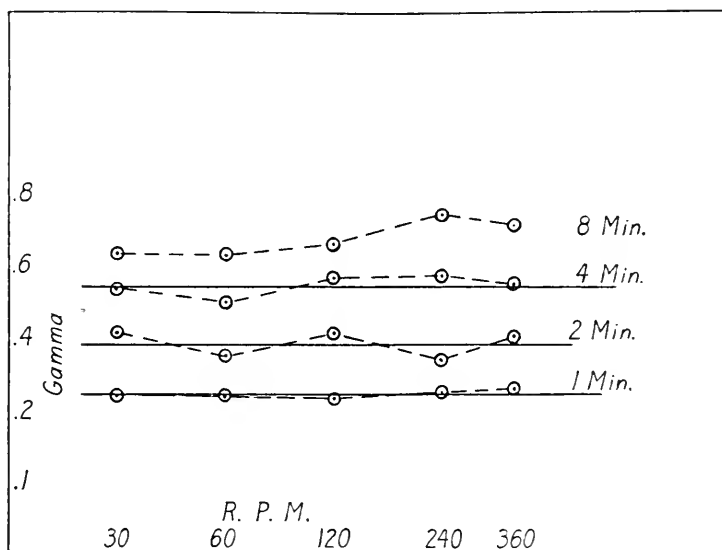


R.P.M.	Velocity.	<i>a</i>	<i>b</i>
30	.32	-1.04	0.21
60	.65	-1.05	0.16
120	1.30	-1.05	0.05
240	2.60	-1.05	0.00
360	4.00	-1.05	0.00

R.P.M.	$\gamma$ 1 min.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.
30	.240	.412	.538	.631
60	.232	.346	.493	.626
120	.227	.411	.562	.660
240	.247	.335	.571	.740
360	.260	.403	.548	.710

FIG. 12.



P-amino-phenol. Experiment 224.



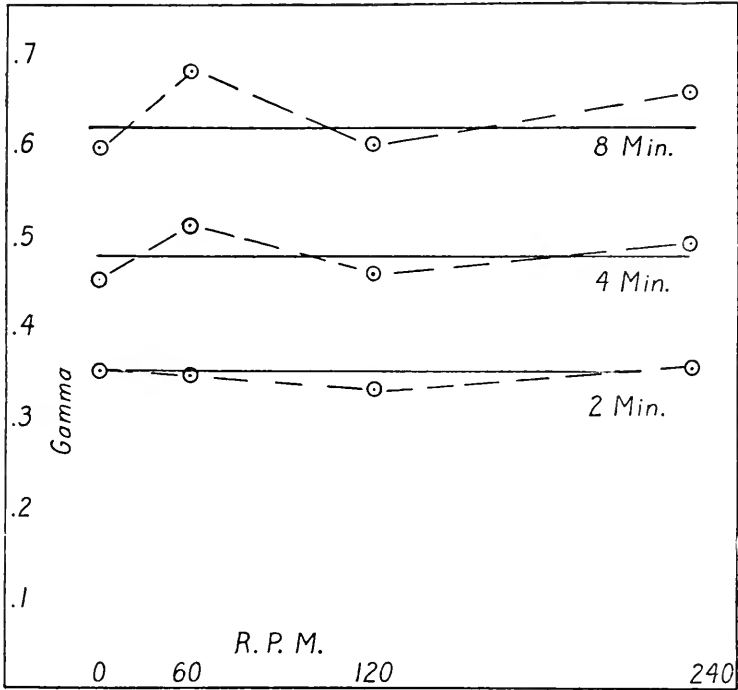
Experiment 227 p-amino-phenol 7.275 gms. = 1/20 molar.

R.P.M.	Velocity.	<i>a</i>	<i>b</i>
30	.32	-1.21	0.20
60	.65	-1.16	0.07
120	1.30	-1.20	0.005
240	2.60	-1.20	0.00
360	4.00	-1.20	0.00

R.P.M.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.
30	.339	.454	.587
60	.338	.517	.686
120	.328	.457	.590
240	.361	.492	.628

FIG. 13.



P-amino-phenol. Experiment 227.

Finally, an experiment was made with a (pyro) developer containing free bromide. This was made with a different batch of emulsion, hence different value of coefficient *a*.

TABLE VI.

R.P.M.	Velocity.	<i>a</i>	<i>b</i>
30	.32	-0.8	.51
60	.65	-0.8	.45
120	1.30	-0.8	.52
240	2.60	-0.8	.50
360	4.00	-0.8	.50



R.P.M.	$\gamma$ 1 min.	$\gamma$ 2 mins.	$\gamma$ 4 mins.	$\gamma$ 8 mins.	$\gamma$ 16 mins.	$\gamma$ 32 mins.
30	.26	.44	.69	1.08	1.10	1.15
60	.21	.38	.61	.85	1.14	1.20
120	.18	.41	.63	.92	1.06	1.20
240	.19	.42	.63	.89	1.17	1.27
360	.15	.33	.57	.90	1.03	1.15
	.20	.40	.63	.93	1.10	1.195

The formula for this developer was as follows:

Pyro	5 grams
K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	4.4 grams
Na <sub>2</sub> SO <sub>3</sub>	16.0 grams
Na <sub>2</sub> CO <sub>3</sub>	18.7 grams
KBr	0.25 grams
Water to	1 litre

#### CONCLUSIONS.

From the results obtained from the very considerable amount of data, it appears that the following conclusions may be drawn, though some qualification may be necessary with other emulsions.<sup>9</sup> It appears generally, within the limits of velocity of stirring used, that the rate of growth of gamma, *i.e.*, the *development velocity*, is largely independent of the rate of stirring. This confirms the conclusion of Sheppard and Mees<sup>10</sup> with ferrous oxalate that "increasing the rotation had but slight effect on the velocity." While this appears generally true, there appears to be a tendency, notably with *pyro* (standard formula) and to a lesser extent with *elon*, for the higher velocities—240 r.p.m. and upwards—to definitely increase the velocity of development. Although the velocities of flow in question—over 2.5 cms. per sec.—are outside ordinary photographic practice, they are not beyond the conditions in continuous development of motion picture film, for which a normal velocity of movement is already 1800 feet/hour = 15 cms. per second. We expect to investigate the effects at these and higher velocities in continuation of the present work. It appears possible that at these higher velocities of stirring some of the complications of the velocity-function of development<sup>11</sup>

<sup>9</sup> The emulsion used was one which independent grain-size analysis [cf. E. P. Wightman and S. E. Sheppard, *J. Phys. Chem.*, **25**, 561 (1921)] showed to have a wide range of grain sizes, hence it is likely to be fairly representative.

<sup>10</sup> *Op. cit.*, p. 58.

<sup>11</sup> Cf. A. H. Nietz, *loc. cit.*



may be considerably reduced. This view is supported by consideration of the influence of stirring velocity upon the coefficients  $a$  and  $b$  of the family of characteristic curves. It will be seen that with hydroquinone-sodium carbonate, a developer of very low reduction potential, there is a progressive change of both  $a$  and  $b$  with increased velocity of flow. The coefficient  $a$  rapidly attains a constant value independent of the velocity of flow, but the  $b$  coefficient shows a more prolonged regression. In Fig. 7 the values of  $a$  and  $b$  have been plotted against the logarithms of the velocities of flow (or r.p.m.). Of the other developers investigated, *pyrogallol* showed only a very slight regression of  $b$ , while *p-amino-phenol* and *elon* show it slightly more.

Provisionally we consider that this effect is a consequence of increased removal of soluble bromide, formed during development, from the emulsion layer. The more pronounced and definite effect with hydroquinone carbonate is in agreement with this view. Nietz has found that the value of  $-b = d$ , the depression of the convergence point due to bromide is given by  $-b = m (\log C - \log C_0)$  where  $m$  is a constant,  $C$  is the concentration of bromide,  $C_0$  the concentration only just producing a depression. On the washing-out hypothesis, the concentration of bromide in the film would be approximately

$$C = n \cdot \left( \frac{1}{V} - \frac{1}{V_0} \right)$$

where  $V$  is the velocity of stirring. Now  $b$  was found to fall off approximately as the logarithm of the stirring velocity, which is therefore in agreement with the view that the bromide in the film is the cause of the effect, which becomes practically negligible when the relatively small amount is washed out as formed and distributed through the whole solution. The only objection to this hypothesis appears to be the following. The normal bromide effect is a consequence of a uniform amount of bromide, independent of the amount of developing image. Under the conditions considered here, the bromide, being formed locally in proportion to the silver developed, might be expected to have a different influence, not shown by a steady definite depression  $b$  of the density. However, in the case of hydroquinone carbonate, there was actually a shift of  $a$ , which is not found with the normal bromide effect, and this may be due to the circumstance just noted. The



explanation offered seems the simplest and most probable, in view of our present knowledge of the dynamics of development.

Finally, it may be noted that the effects observed, particularly when intensified by other factors, such as developer exhaustion, etc., account for part of the anomalies sometimes encountered by workers in photographic sensitometry.

#### SUMMARY.

1. An apparatus is described for uniform development of sensitometric strips on film at various velocities of stirring (30 to 400 r.p.m.).

2. Results obtained with hydroquinone, pyrogallol, p-aminophenol, and elon developers are given in tables and graphically.

3. It is found that the velocity of development, as rate of growth of  $\gamma$ , is little affected by rates of flow up to 4 cms. per second.

4. With hydroquinone carbonate at low stirring velocity an effect like bromide depression (induction) was observed; this is removed as the stirring velocity is increased. The effect (induction) with other developers used was small or negligible.

5. This regression is attributed to improved removal of soluble bromide from the film with increased velocity of stirring.

---

**Heavy Fuel Oils in Internal Combustion Engines.**—This problem is the subject of a paper recently read by Harold Moore, M.Sc., before the North-East Coast Institution of Engineers and Shipbuilders, at Newcastle-on-Tyne.

The difficulties in burning heavy oil are of three types: Ignition, burning after ignition, impurities. These types are distinct. Oils may be found satisfactory in two respects, but unfit for use on account of the other defect. Heavy-oil engines are classified by the author in three groups: Diesel engines, using compressed air for firing; cold-starting engines which fire by spontaneous combustion, the fuel being pulverized without air blast; hot-bulb engines, in which the fuel is injected mechanically, external heat being applied to ensure ignition. The capacity of an engine for burning heavy fuels is not merely dependent upon the cycle and method of fuel injection; it is also dependent to a very marked extent upon the size, speed, compression, fuel-valve tuning and other factors.

The chemistry and physics of the difficulties are presented in much detail and remedies are pointed out. The paper is quite extensive and covers a subject of great importance on power industry. H. L.



# RESISTIVITY OF VITREOUS MATERIALS.\*

BY

L. L. HOLLADAY,

Physicist, Laboratory of Applied Science, Nela Research Laboratories.

ABOUT a year ago the writer investigated the resistivity of various types of glasses and found that all the results seemed to follow a general law, which apparently had not been heretofore recognized.

It is well known that the resistivities of glasses and other similar substances are high at room temperatures and that they decrease greatly as temperatures near their softening points are approached. Indeed the changes are so great that the resistivities are frequently expressed and plotted logarithmically.

In making our tests upon the resistivity of glass, several methods of test were made necessary by the fact that the range of resistivity values cold and hot were in about the ratio of  $10^{13}$  to one. All our measurements were made upon glass tubes about one-half inch outside diameter. At temperatures from  $20^{\circ}$  to  $75^{\circ}$  C. measurements were taken with the current traversing the walls of the tube radially by sealing one end of the tube and placing it in a conducting bath, and filling it with some of this same liquid. The current through the glass was measured with a very sensitive galvanometer.

At higher temperatures the measurements were taken with the current traversing the walls of the tube longitudinally and the current measured with a potentiometer: the tube was suspended within an electric furnace which was constructed for uniform temperature throughout the region occupied by the glass specimen, the temperature being measured by a standardized thermocouple. Electrical connections were made to the glass specimen first by electroplating a band of copper around each end; and later, by fusing wires, having about the same coefficient of expansion as glass, into the ends of the tube.

During this investigation eleven specimens of glass were tested through a temperature range of about  $20^{\circ}$  to  $500^{\circ}$  C. and

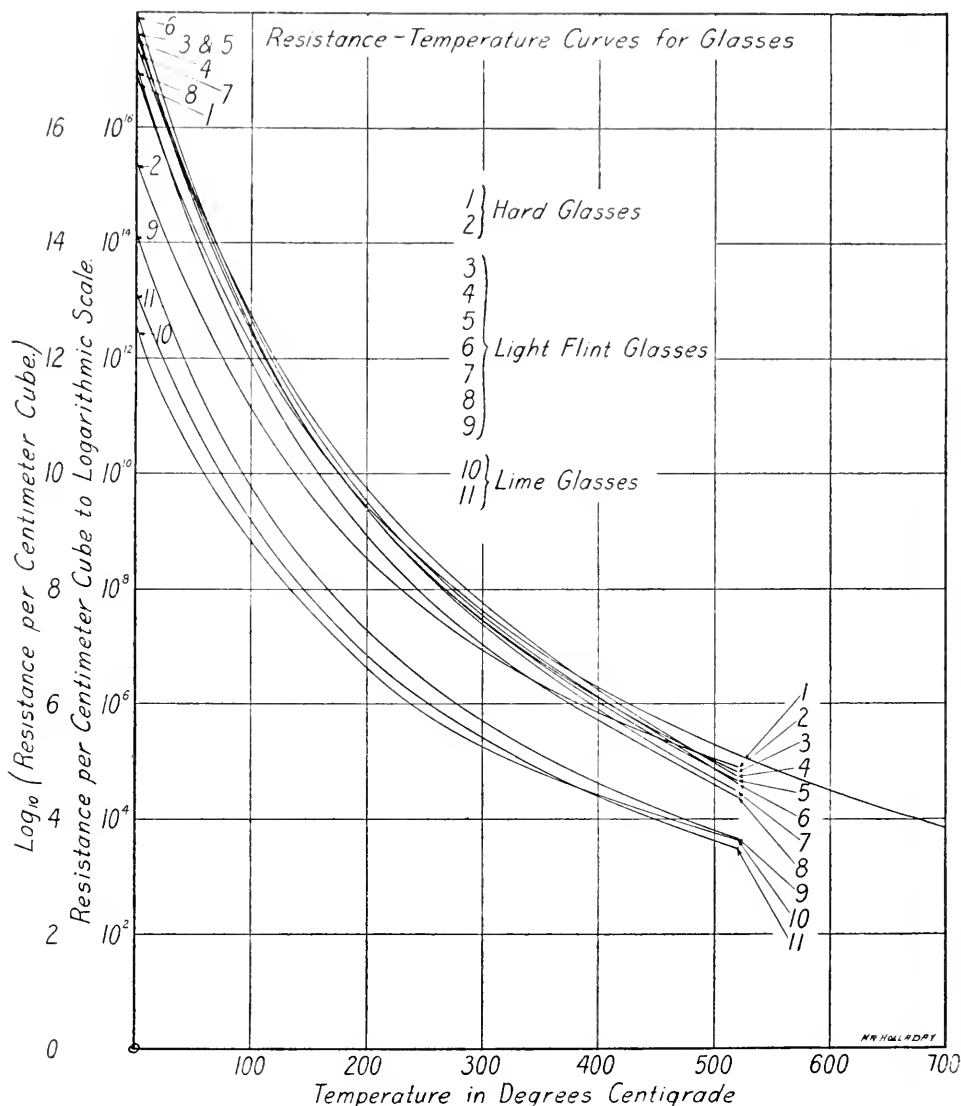
---

\* Communicated by the Director of the Laboratory.



the results plotted. For each specimen of glass the results were plotted, the logarithm of resistivity being plotted against temperature. Through these points a smooth curve was drawn. Fig. 1 shows a summary plot for the eleven specimens. Were

FIG. 1.



absolute temperature used instead of Centigrade, the curves would be more or less asymptotic to the two axes. When the logarithm of resistivity for a given specimen is plotted against the reciprocal of absolute temperature the curve is practically a straight line which projected intersects the temperature axis close to the origin. A summary plot of these results is given in Fig. 2.



An empirical formula satisfying the experimental results for each specimen was derived, and all were found to be of the following general form

$$\text{Log}_e (R) - x \log_e (T) = \frac{Q}{T} - \log_e (P)$$

The equation for resistivity  $R$  may therefore be written

$$R = \frac{T^x}{P} \varepsilon^{\frac{Q}{T}}$$

and the corresponding equation for conductivity is  $K = \frac{P}{T^x} \varepsilon^{-\frac{Q}{T}}$

where  $P$ ,  $Q$ , and  $x$  are constants, and  $\varepsilon$  is the base of natural logarithms.

For specimens Nos. 1, 3, 4, 5, 6, 7, and 8 a few more of the points fell below the straight line than above at the ends when the logarithm of resistivity was plotted against the reciprocal of temperature; thus indicating that  $x$  had a negative value of about one-half. However, owing to different methods of measuring the resistivity at high and low temperatures and owing to the experimental difficulties of measuring at the two extremes of the temperature range, it is not certain that the curves in these cases are straight lines. Fig. 3 has been prepared to illustrate the slight change in the shape of the curve that is effected by assuming that  $x$  is equal to plus or minus one. The three curves pass through the common points corresponding to the temperature of  $323^\circ \text{K}$ . and  $723^\circ \text{K}$ .

For practical purposes it is satisfactory to assume that  $x$  is equal to zero, for by so doing a resistivity-temperature curve may be drawn when the resistivities at but two temperatures have been measured. However, it is believed that the equation  $R = \frac{T^{-1/2}}{P} \varepsilon^{\frac{Q}{T}}$  more nearly fits the average results.

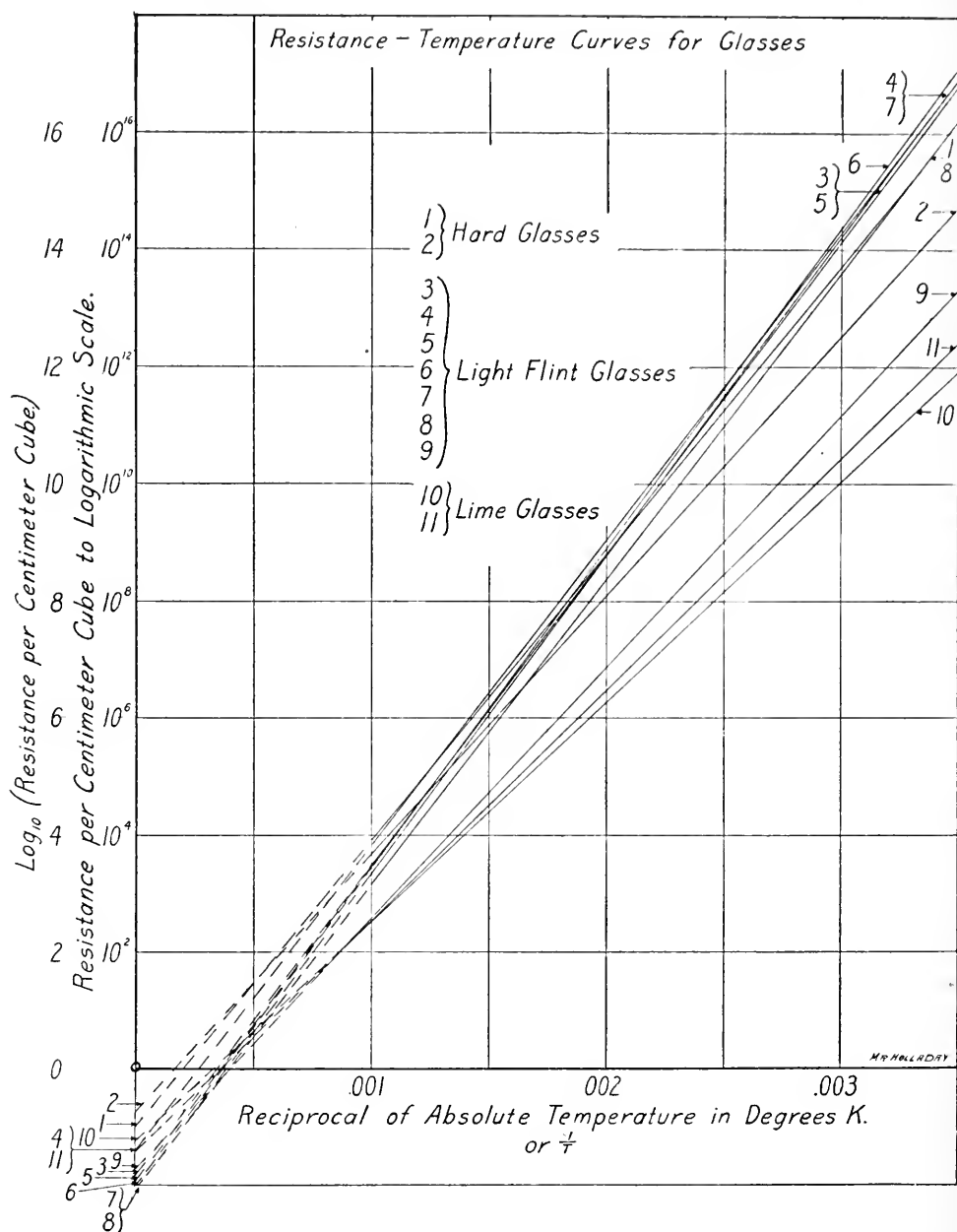
An explanation of our observed results may probably be most simply found by employing Maxwell's law of distribution of molecular velocities.

Since glass is an amorphous substance with presumably no crystalline structure, free electrons would probably encounter about the same kind of resistances to their movement that they do in an ordinary gas, and would be acted upon by the electric forces of ionized molecules and other electrons about as in a gas.



As a concrete example of this, J. C. Ghosh<sup>1</sup> showed that in a solution of strong electrolytes the proportion of dissolved

FIG. 2.



molecules which are dissociated and yield free ions for the production of current is  $\epsilon \frac{A}{nRT}$ , where  $\frac{A}{nR}$  is proportional to the work expended in removing an ion out of the sphere of influence

<sup>1</sup> Chem. Soc. J. Trans., 113, pp. 449-458, May, 1915.



of neighboring ions. By the application of this formula he was enabled to calculate the conductivity of binary electrolytes to within 1 per cent. of observed values. When we assume that instead of  $n$  being the number of ions into which a molecule dissociates, it is the number of electrons and charged molecules formed by the ionization of the glass molecules, and when in addition we assume suitable data for glass we obtain a value for  $Q$  of the same order of magnitude as the ones given in the accompanying table calculated from observed data.

Following the striking discoveries of super-conductivity by K. Onnes, O. W. Richardson,<sup>2</sup> by employing the theory of doublets, advanced by J. J. Thomson, gave the conductivity of a metal when its temperature is sufficiently high for the specific heats of the metal to become normal as follows:

$$K = \frac{1}{3} \frac{NepdM}{kT},$$

where  $N$  is the number of doublets in unit volume,  $M$  the moment of a doublet,  $e$  the electronic charge,  $p$  the number of times an atom emits an electron per second,  $d$  the distance between the centres of adjacent atoms,  $k$  Boltzmann's constant, and  $T$  the absolute temperature. Also assuming that free electrons obey Maxwell's law of distribution of velocities and other gas laws, he showed that the ratio of the total number of electrons that start to the surface to the number that actually escape is

$$\frac{1}{\sqrt{\pi}} \sqrt{\frac{kT}{w}} e^{-\frac{w}{kT}}$$

where  $w$  is the work done by an electron in escaping from the surface. If we assume that the surface be the sphere of influence of other electrons and atoms, we have an analogy to J. C. Ghosh's demonstration for electrolytes. Now assuming that the above ratio is proportional to  $p$  the number of times an atom emits an electron per second, we have for conductivity

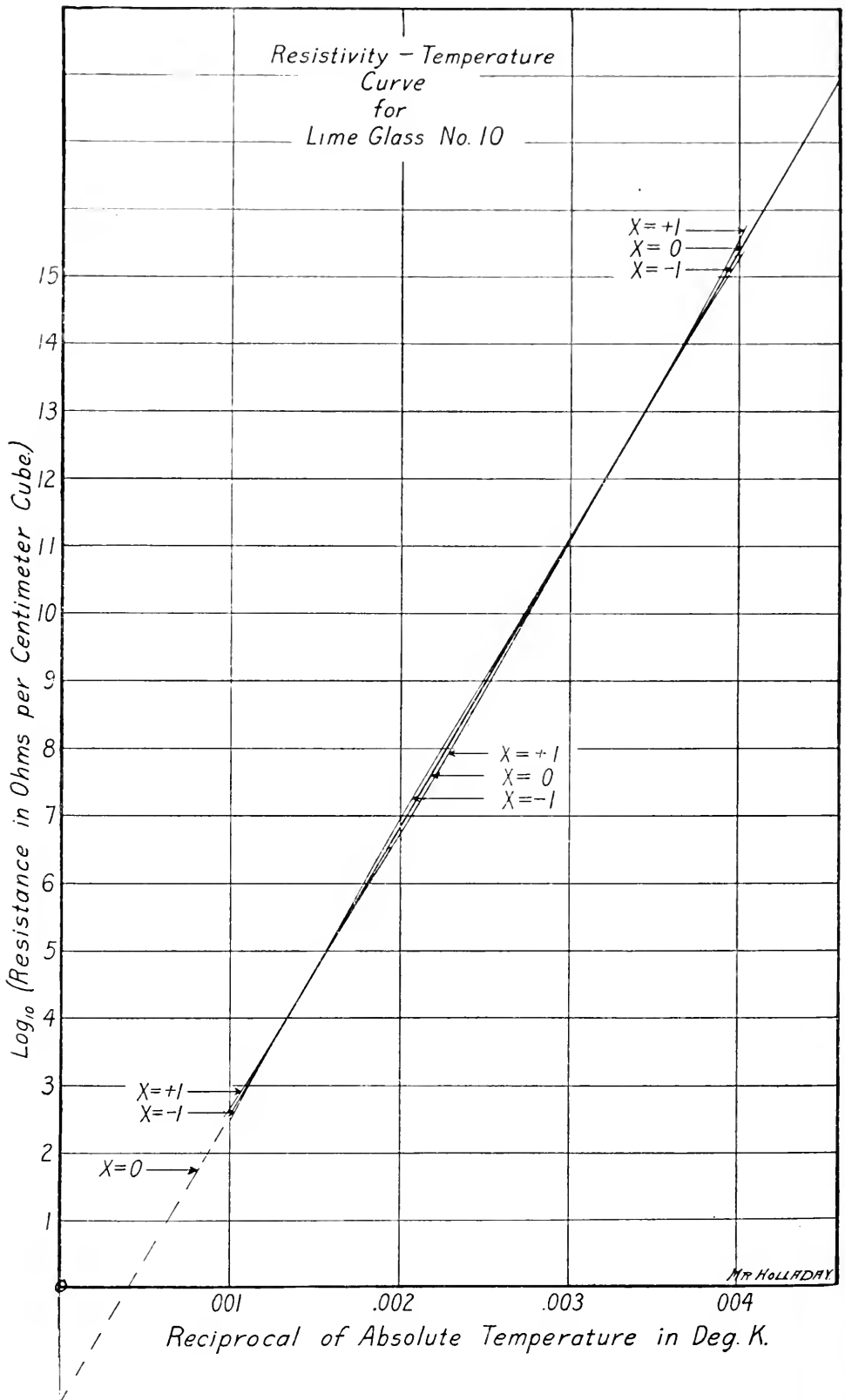
$$K \propto \frac{1}{3} \frac{NedM}{kT} \frac{1}{\sqrt{\pi}} \sqrt{\frac{kT}{w}} e^{-\frac{w}{kT}}$$

---

<sup>2</sup> *Phil. Mag.*, 30, 1915, p. 295.



FIG. 3.





Or assuming that  $N$ ,  $d$ , and  $M$  are constant, the expression for conductivity becomes

$$K = \frac{P}{\sqrt{T}} \epsilon^{-\frac{Q}{T}}$$

On the other hand, if  $M$  varies as  $T^{-\frac{3}{2}}$ , which Richardson states will make it accord with thermodynamical requirements, our equation for conductivity becomes

$$K = \frac{P}{T^2} \epsilon^{-\frac{Q}{T}}$$

It is the writer's belief that this equation does not accord with the experimental data as well as the former equation.

In conclusion it may be stated that experimental results show and theory indicates that the conductivity of vitreous substances varies according to absolute temperature  $T$  as  $\epsilon^{-\frac{Q}{T}}$ . And theory indicates that conductivity may also vary with temperature as  $T^{-\frac{1}{2}}$  or as  $T^{-2}$ ; but throughout the working range of temperature for glasses it is practically immaterial which exponent is employed.

From the observed values of  $R$  for several glasses, values of  $P$  and  $Q$  have been estimated and tabulated below for assumed values of  $x$  equal to  $+\frac{1}{2}$  and zero.

Type of Glass.		No.	VALUES OF CONSTANTS			
			For $X = + \frac{1}{2}$		For $X = 0$	
			P	Q	P	Q
Hard Glass	.....	1	453	11,630	9.1	11,280
Hard Glass	.....	2	157	10,280	5.7	10,160
Light Flint Glass	.....	3	2,291	12,430	74.1	12,270
Light Flint Glass	.....	5	2,870	12,510	84.1	12,340
Light Flint Glass	.....	7	8,091	12,970	99.5	12,400
Light Flint Glass	.....	9	1,807	10,040	49.	9,790
Lime Glass	.....	10	1,145	9,370	23.7	9,050

**Thermal Analysis at Low Temperatures.** F. E. E. GERMANN. (*Phys. Rev.*, June, 1922.)—Solutions of uranyl nitrate were heated and cooled between the temperatures of melting ice and of a mixture of ether with solid carbon dioxide. A thermo-electric junction of copper-advance placed in the solution enabled the temperatures of the latter to be followed. The common course of temperature changes was the following: For a brief time the solution fell in



temperature, then it rose for an even shorter time until the whole mass was a solid mixture of ice and uranyl nitrate hexahydrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . After this for a much longer time the temperature grows less. This is succeeded by an interval, when it suddenly rises through a considerable number of degrees. After this there is a continuous fall of temperature. A study of solutions of varying concentration showed that the maximum amount of heat evolved during the second and more important rise of temperature is displayed in a solution containing 48 per cent. of uranyl nitrate. When the specimen, the cooling curve of which was described above, is heated up, the temperature rises to a certain point and then remains almost constant for a time while heat is being absorbed. Subsequently a rise of temperature follows.

These observations are interpreted to indicate that a new hydrate, the icositetrahydrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , is formed at about  $-35^\circ$ . This decomposes spontaneously at  $-20^\circ$ .

"When a water solution of uranyl nitrate is cooled to the temperature of liquid air, it is possible to get a distinct fluorescent spectra from it, depending in general on the rate of cooling. H. L. Howes has described what seemed to him to be five distinct spectra, varying from a sharp line spectra in the case of slow cooling to a broad-banded spectrum in the event that the solution was plunging directly into liquid air. The other spectra were the results of other chance intermediate methods. As far as we know to-day, the emission and absorption spectra of elements and compounds are very characteristic at any given temperature, so that it would seem quite impossible to obtain more than one fluorescent spectrum for a given compound." The inferred existence of the new hydrate goes far to explain how so many spectra can be emitted.

G. F. S.

**On Reflection from a Moving Mirror and the Michelson-Morley Experiment.** E. H. KENNARD and D. E. RICHMOND. (*Phys. Rev.*, June, 1922.)—The results of the celebrated Michelson-Morley experiment are usually interpreted in such a manner that they form the very foundation of the Theory of Relativity. As a consequence of the constantly increasing range of this theory the underlying experiment has been subjected to close scrutiny. Righi has done this and has attacked the common explanation of the results. This is, on the other hand, defended by Villey. The two authors approach the problem afresh. They are particularly concerned with a second-order term which, in Righi's opinion, is adequate to explain why the experiment gave only a negative result. They conclude that this troublesome term would not change to a perceptible extent the pattern of interference fringes. "It appears certain therefore that the famous negative result of Michelson and Morley was not due to any second-order effect of motion upon reflection at the mirrors." "The usual interpretation of the experiment in favor of Relativity still holds."

G. F. S.



## NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

### ANNUAL REPORT OF THE DIRECTOR OF THE BUREAU OF STANDARDS, 1922.<sup>1</sup>

[ABSTRACT.]

THE outstanding feature of the fiscal year ended June 30, 1922, as far as the Bureau of Standards of the Department of Commerce is concerned, was the great amount of attention paid to industrial standardization, to the elimination of waste in the industries, and to the simplification of industrial products. While fully as much time and attention has been paid to fundamental measurements as heretofore, these have all been carried out with the particular idea of their importance in some definite line of work. It is gratifying to note that in all the important researches which have been undertaken, the Bureau has had the hearty coöperation of American manufacturers. Their aid has been invaluable in the solution of industrial problems, and it is believed that the cordial relations which now exist between the Bureau and the industries will continue in the future.

The number of tests completed during the year include 62,104 for the Government, 30,464 for the public, representing a value of \$345,001.05. The personnel of the Bureau has been made up of 342 statutory employees and 546 engaged in special research.

In connection with weights and measures, a great deal of attention has been paid to the improvement of the apparatus with which such work is conducted. Very satisfactory comparisons were made between the fundamental standards of the Bureau and sets of high precision weights showing that the accuracy of the standards has not been decreased over a long period of time. An important development was the recognition by the Bureau of a special specific gravity scale for the petroleum industry, and the Bureau's agreement to certify apparatus according to this scale.

Very satisfactory progress was made in testing railroad track scales, and a considerable improvement has been noted in their accuracy. The mine scale work, however, was greatly interfered

---

\* Communicated by the Director.

<sup>1</sup> Miscellaneous Publication, No. 50.



with by the strike in that industry. The Fifteenth Annual Conference on Weights and Measures was particularly successful and several notable speakers, including the Secretary of Commerce, took part at the meetings.

In the field of electricity, many important accomplishments may be recorded. The year has been marked by an unprecedented increase of popular interest in radio, and to meet the demand the Bureau has issued a number of publications treating with this subject in a more or less elementary way. It has also aided in the testing of radio apparatus.

An important conference was held at the Bureau at which standard specifications were prepared covering all classes of dry cells. As a result of the adoption of these specifications, the number of sizes of cells which dealers must keep in stock will be greatly reduced.

Investigations to determine better ways for utilizing natural and artificial gas in industrial and domestic appliances have been carried out, and several publications have been issued on this subject.

Quite a change was noted in the type of clinical thermometers submitted for test. During the past year over 90 per cent. of such thermometers were for human use as compared with but 5 per cent. last year. A steady movement may be noted tending toward the rigid testing of all such thermometers which are sold, and it seems probable that the Federal Government will be asked to aid in this work.

Very elaborate investigations covering a long period resulted last year in the preparation of tables giving the thermodynamic properties of ammonia, the most complete work of the sort that has ever been carried out.

In connection with the testing of internal combustion engines, particular attention has been paid to road tests of automobiles and special apparatus has been designed which will give the performance of any type of car under service conditions.

In the field of optics, many important results have been achieved. The Bureau's figures for the length of the cadmium red line as a fundamental standard of wave-length have been adopted by the International Astronomical Union. Measurements have been made of the radiation of a large number of stars using apparatus specially designed by the Bureau.



Close coöperation has continued between the Bureau and the sugar industry, and with the very complete apparatus now in the Bureau's laboratories even more important results may be expected.

During the year special attention has been paid to a study of nickel deposition with the hope that those conditions of operation which will yield the most satisfactory results with the least expense and loss can be defined.

Many different kinds of balloon fabrics have been tested, and a method for showing the purity of gas in a balloon without the necessity of drawing any of the gas from the balloon has been developed.

Important work in coöperation with British, Scotch, and Italian analysts has been carried out on standard pure metals.

Work in connection with the sound transmitting properties of building materials has been continued during the year, and a special sound chamber where such measurements may be carried out has been completed. Also a new and larger wind-tunnel was put in service giving the Bureau exceptionally fine equipment for aerodynamical work. A large number of aeronautic instruments have been tested and designed to meet special requirements, nearly all this work having been conducted in coöperation with the Army and Navy Air Services.

In the field of structural materials, a fundamental investigation is under way on the theory of columns as well as on the fatigue resistance of metals. Other work in progress includes an investigation of the use of concrete for houses and inspection of such structures already in existence.

An endurance testing machine for automobile tires has been completed, and the special apparatus for measuring power loss in tires has been in almost constant use. A publication was issued on the durability of sole leather prepared by two different methods, and in the field of textiles very important work, much of which was of a coöperative character with textile organizations, has been carried out. One of the principal investigations conducted during the year was on the heat-retaining properties of blankets.

Work which will eventually lead to the standardization of paper sizes is well under way, and, as in the case of textiles, important coöperative work along many lines may be recorded.



Important metallurgical investigations have included a study of methods for the analysis of gases in metals, the determination of thermal stresses in car wheels, and the rust resistance of alloy steels. Particularly important work has been accomplished by the research associates in metallurgy sent to the Bureau by various manufacturers.

As in other work, in connection with ceramics the practical problems have been particularly stressed. Tests have been conducted of tableware and window glass, the best types of American clays to use in paper-making have been determined, and the comparative value of various ceramic materials for different purposes has been investigated.

The making of optical glass in the Bureau's laboratory has been carried on very successfully, a great deal of first-class glass in the form of lens blanks and finished lenses having been supplied to other branches of the government, particularly the Navy Department.

Specifications are being prepared for refractories, such as the fire brick in boiler furnaces, and work is under way which will lead to the improvement of enamelled metal products.

New and important work undertaken during the year was that in connection with building and housing, and several publications covering the current prices of building materials, the questions relating to zoning, and dealing with the preparation of building codes have been issued.

In connection with simplification and the elimination of useless sizes, the important work resulting in the standardization of paving brick may be mentioned.

---

#### FIFTEENTH ANNUAL CONFERENCE ON THE WEIGHTS AND MEASURES OF THE UNITED STATES.<sup>2</sup>

THE Annual Conference on Weights and Measures is an unofficial body composed of state and local officials, concerned with the enforcement of weights and measures laws and ordinances, which meets once in each year to consider and solve problems arising in connection with their work. This publication is a report of the fifteenth meeting of this conference, which was attended by about 185 persons from 28 states, including officials, railroad scale men, manufacturers' representatives and others in-

---

<sup>2</sup> Miscellaneous Publication, No. 51.



terested. Addresses were given by the Secretary of Commerce, Hon. Herbert Hoover, and by the Chairman of the Committee on Coinage, Weights and Measures, Hon. A. H. Vestal, of Indiana. Perhaps the most important single subject discussed was tolerances on heavy-duty automatic scales. Very many of these scales have been put in use in the past few years and the subject of tolerances is one of very great importance. A report on the accuracy of these scales in service based on a comprehensive field investigation made by the Bureau of Standards and the Committee on Specifications and Tolerances of the Conference, was presented, as was a progress report of the Committee outlining the factors on which the tolerances should be based and suggesting tentative figures. This report was accepted and will form the basis of a further study of the subject by interested parties throughout the country. Tolerances were tentatively adopted on linear-measuring devices while tolerances on bread loaves were discussed and a committee appointed to meet with a like committee of the baking industry to consider the whole subject of uniform laws and tolerances. Other subjects of interest were methods of test of gasoline pumps, linear-measuring and leather-measuring devices, wholesale deliveries of gasoline, sale of dry commodities by weight, Federal and State approval of type of apparatus, relationship between manufacturers, merchants, and officials, a uniform ton for coal, uniform requirements for milk bottles, protection of highways by portable weighing devices, etc.

---

**THE STRUCTURE OF MARTENSITIC CARBON STEELS AND  
THE CHANGES IN MICROSTRUCTURE WHICH OCCUR  
UPON TEMPERING.<sup>3</sup>**

By H. S. Rawdon and S. Epstein.

[ABSTRACT.]

IN spite of the information afforded by recent investigations concerning the nature of the transformation changes in iron and steel, there still remains much to be learned concerning the visible structural features of martensite and the changes which occur upon tempering. A study of the microstructure of hardened and tempered carbon steels was carried out on a series of six steels varying from 0.07 to 1.12 per cent. carbon. These were hardened

---

<sup>3</sup> *Scientific Papers*, No. 452.



by water-quenching from different temperatures ranging from 750 to 1250° C. The effect of heating previous to quenching was also considered. The results produced by tempering were studied in hardened specimens reheated to temperatures varying from 100 to 650° C., consideration being given to the length of time the specimen was reheated. The investigation consisted largely in microscopic examination, supplemented by a study of the scleroscope hardness of the quenched and of the tempered steels.

The coarseness of the martensitic structure appears to be determined almost entirely by the temperature from which the material is quenched; the influence of the period during which the material is heated previous to quenching, at least up to four hours, is relatively very slight as compared with that of temperature.

Each crystal of austenite of the hot steel is transformed during the quenching into a system of martensitic plates or needles, the orientation of the system from any austenite being quite distinct from that produced from the neighboring ones. Martensite is formed from austenite in a manner analogous to the freezing of a solid-solution alloy, in that each of the chemically homogeneous austenite crystals gives rise to a structure that is non-homogeneous in composition. A redistribution of carbon takes place and the conspicuous martensite plates or needles are found to be distinctly lower in carbon than the "filling material." Evidence of this may be obtained from the characteristic behavior of the specimen after complete tempering, toward etching reagents. The enrichment in carbon of the filling material between the needles may be great enough so as to allow small patches of austenite to persist in the steel after quenching. Both the 0.85 C. and 1.12 C. steels showed austenite, particularly in specimens quenched from the highest temperatures. None of the other steels showed any features, however, which suggested the retention of austenite after quenching.

The changes which occur during tempering are considered under two headings: Those below and those above 250° C. The structural changes below this temperature are relatively slight and manifest themselves by the difference in the rate of etching of martensite, particularly in the steels of high-carbon content, with respect to alkaline oxidizing reagents.



By means of liquid-air treatment, it was shown that low-temperature tempering has only slight effect upon the austenite retained in high-carbon steels after quenching. Between 200 and 250° C., however, it is transformed entirely and disappears as a constituent of the microstructure in steels tempered to 250° or above.

A relatively pronounced change in structure of hardened steels occurs at approximately 250°. The martensite and austenite, if present, are transformed and the steel begins to assume a granular appearance. The rate of etching in acid reagents increases very rapidly soon after this tempering temperature has been reached. Further tempering increases the granular structure so that after heating at approximately 500° C. the individual particles of cementite may be detected under the microscope. Fully tempered steels, after being etched with a reagent which colors the cementite particles, show the unhomogeneity in composition, which resulted from the redistribution of carbon which occurred during martensite formation.

The curves summarizing the scleroscope hardness of steels tempered at various temperatures show a distinct change of slope at approximately to 250° C. Below this temperature the hardness decreases very slightly as compared with the rate of decrease above 250° C. In the steel of highest carbon content used the hardness number after a long tempering period below 250° C. was distinctly higher than after a short tempering at the same temperature. The hardening resulting from the gradual change in the austenite neutralizes to some extent the softening in the martensite which occurs readily upon tempering even at low temperatures. None of the tempered specimens, however, showed a hardness number greater than that of the initial hardness directly after quenching, as has been reported by some investigators.

An increase in the temperature from which the steels were quenched, provided this was above the  $A_{c_1}$  transformation, or a long heating period previous to quenching produces no marked effect upon the scleroscope hardness of the quenched steel.

The evidence afforded by the investigation did not appear to warrant any speculative discussion concerning the ultimate nature of martensite, although several important features were revealed, which must be accounted for in any explanation of the real nature of this constituent.



THE ACTION OF CHARRED PAPER ON THE PHOTOGRAPHIC  
PLATE AND A METHOD OF DECIPHERING  
CHARRED RECORDS.<sup>4</sup>

By Raymond Davis.

[ABSTRACT.]

THE Bureau of Standards was recently called upon to find a method for deciphering the written and printed matter contained on charred paper.

The charred papers submitted apparently had been subjected to heat in a closed vessel, such as a safe—the paper having been converted into black sheets of carbon and not to ashes as would have been the case had they been burned in an open container.

With casual observation no traces of writing are visible, but under certain critical conditions of lighting very faint traces of markings can be seen. These traces are not sufficiently clear to permit deciphering.

In some preliminary trials made on paper charred for the purpose, conversion of the iron salts contained in the ink into colored salts was tried. These were unsuccessful.

It is known that the photographic plate, besides being sensitive to light, is also sensitive to certain gases and vapors. Some of these have the property of fogging or rendering developable such portions of the plate as are exposed to their actions. Certain other gases or vapors have the contrary property, that is, they partially or completely desensitize the plate.

For the first trial a sheet of the carbonized paper was placed between two "fast" photographic plates and kept in the dark for two weeks. On development in the usual manner a very perfect copy of both the writing and the printing was obtained. It appears that the carbonized paper contains gases that fog the photographic plate. Where the ink is present, little or no effect takes place. Apparently the ink acts as a screen, hindering the escape of the gas.

It is interesting to note that the writing on both sides of the charred paper appears, that from the back being fainter than that from the face. Apparently the ink penetrates the paper sufficiently so that its residue reduces the amount of gas escaping from beneath.

---

<sup>4</sup> *Scientific Papers*, No. 454.



No attempt was made to determine the nature of the active material contained in the charred paper. It is quite likely that it contains products similar to those obtained by the destructive distillation of wood.

Further tests showed that photographic plates of sensitiveness usually termed fast or medium are best adapted for this purpose. However, the sensitiveness to light is no definite indication of the sensitiveness to the charred paper. For example, Seed 30 and Seed 26X are of equal sensitiveness to the charred paper, the former is considerably faster to light than the latter. Very slow plates, such as "Process" are not suitable as exposure of thirty-two days shows only faint action. Photographic printing and enlarging papers are very insensitive to the charred paper.

Results obtained by the use of photographic films were very surprising, as shown by the two types of emulsions selected for the test, namely, Eastman "Portrait Film" and Eastman "Super Speed Portrait Film."

The Portrait Film showed no effect in thirty-two days. The Super Speed Portrait showed very slight but interesting effect with a sixteen-day exposure and only a little better at thirty-two days. This was just the reverse of that with the plates, the inked areas showing black on the films, whereas on the plates they show clear. That is, with the films the ink is the active portion, the charred paper produces no fogging. It was also noted that the chemical fog of development is much lighter over the portions of the film covered by the charred paper as compared with the uncovered areas.

The results suggest that there are perhaps two different kinds of gas given off, one kind by the charred paper and another by the ink, both of which fog the photographic emulsion, but the one from the charred paper more rapidly.

It was found that after a short washing these films in distilled water, for about five minutes, followed by thorough drying, gave results similar to those obtained with plates. Very good copies were obtained from washed film after eight days' contact with the charred paper.

Separate sheets of the charred paper which had been exposed to the air for several months required two weeks' contact with the photographic plate to produce a good printing negative, whereas sheets taken from a charred ledger required only one week to give



an equally good negative. It is natural to assume that the active material is gradually lost by exposure to air—the activity having dropped one-half in about two months' time. Following this, however, the rate of depletion has dropped considerably, no further reduction in activity having been observed.

---

**TABLES FOR THE CALCULATION OF THE INDUCTANCE OF  
CIRCULAR COILS OF RECTANGULAR CROSS-SECTION.<sup>5</sup>**

By Frederick W. Grover.

[ABSTRACT.]

MULTIPLE-LAYER coils are much used where a larger inductance is required than can conveniently be obtained from a single-layer coil. To reduce the considerable capacity which is associated with a simple circular coil wound in layers in a channel of rectangular cross-section, recourse is had to "banked" windings, or the layers may be spaced apart by small thicknesses of insulating material, or a "honeycomb" type of winding may be employed.

In all these cases, the inductance may be calculated with a good degree of accuracy by the formulas which apply to a circular coil with the current uniformity distributed over a rectangular cross-section. For this purpose the dimensions of that ideal coil of this type which is equivalent to the actual coil must be used. For the dimensions of cross-section there should be taken the product of the winding pitch in the layer by the number of turns in the layer for one dimension, and for the other the product of the distance between corresponding turns in successive layers by the number of layers. The mean radius of the equivalent coil is the same as the mean radius of the actual coil. Thus, the rectangular cross-section of the equivalent coil may be imagined to be made up of a rectangular array of equal smaller rectangles, with a turn of the wire of the coil at the centre of each. The inductance of the actual coil differs, of course, from that of the equivalent coil by a small amount, for which a correction may be calculated as shown by Rosa.

A number of formulas have been developed in the past for calculating the inductance of a circular coil of rectangular cross-section. Of these especial mention may be made of the formulas of Lyle, Dwight, and Butterworth, which between them cover

---

<sup>5</sup> *Scientific Papers*, No. 455.



all possible coils of this type. These formulas are, however, somewhat complicated, and calculations by them are tedious and time consuming. Furthermore, the computer is likely to experience some uncertainty in certain cases in the choice of the most suitable formula for his problem. If many calculations have to be made, some means of reducing the labor of computation and for doing away with the necessity of choosing among the formulas is a practical necessity.

Several solutions of this problem have appeared in recent years. Of these there may be mentioned the single empirical formula of Brooks and Turner, which gives an accuracy of from 1 to 3 per cent. in different cases, and the curves of Coursey and Dwight. The values calculated by Coursey for *thick* coils give only a rough accuracy on account of the formula used being unsuited for this case. Neither of these sets of curves as reproduced by the printer allow of an accuracy of better than 1 per cent. in the value of the inductance.

The tables presented in this paper are calculated from the accurate formulas cited above, more than one formula having been used wherever this was possible as a check on the results. The tabulated values are correct to a part in ten thousand, and even where a double interpolation has to be made, the error is less than one part in a thousand. If desired, curves can of course be constructed from the data of the tables, with, however, a sacrifice in accuracy.

The inductance may be calculated by either or both of the following formulas:

$$L = 0.002 \pi^2 n^2 a \frac{2a}{b} K' \text{ microhenries} \quad (1)$$

or

$$L = 0.001 n^2 a P' \text{ microhenries,} \quad (2)$$

in which

$a$  = the mean radius of the equivalent coil,

$b$  = the axial length of the equivalent coil,

$c$  = the radial thickness of the equivalent coil,

$n$  = the number of turns,

and  $K'$  and  $P'$  are quantities which are given in the tables as functions of the two parameters  $c/2a$  = thickness divided by mean diameter and  $\frac{c}{b}$  or  $\frac{b}{c}$ , the shape ratio of the cross-section.



Formula 1 is especially suited to long, thin coils, while 2 is better adapted to pancake coils or coils of nearly square cross-section. Either may be used, however, in any case, and thus a check on the numerical work is afforded.

Where interpolation has to be made in the tables, a greater accuracy is obtained if in 1 we write  $K' = K - k$ , and obtain from the tables the values of  $K$  and  $k$  separately.  $K$  is Nagaoka's constant, the value of  $K'$ , which applies to a cylindrical current sheet or coil with  $c = 0$ . Similarly, in the case of 2 it is more accurate to put  $P' = Pf$  and to interpolate for  $P$  and  $f$  separately.  $P$  is the value of  $P'$  which applies to a disk coil of zero axial thickness,  $b = 0$ , and is tabulated here from Spielrein's formula as a function of  $\frac{c}{2a}$ .

Examples are given to illustrate the use of the tables and formulas in practical cases, and the application of the tables to the calculation of the mutual inductance of coils of rectangular cross-section is treated and illustrated and the necessary formulas developed.

The formulas on which the tables are based are collected for reference in an appendix.

---

### SPECTROPHOTOELECTRICAL SENSITIVITY OF SOME HALIDE SALTS OF THALLIUM, LEAD, AND SILVER.<sup>o</sup>

By W. W. Coblentz and J. F. Eckford.

[ABSTRACT.]

THIS paper, considered in connection with previous publications (*Sci. Papers*, No. 446 and one, on press), completes a study of the effect of crystal structure, chemical constitution, and atomic weight upon spectrophotoelectrical sensitivity. It is shown that these factors have a definite effect upon the photoelectrical reaction just as previously they were found to have a specific effect upon absorption and reflection spectra.

It was found that the spectrophotoelectrical reaction of the halide salts of thallium, lead, and silver is confined to a very narrow region of the violet end of the spectrum, being the narrowest and most sharply defined reaction spectra of all substances yet published, including the photoelectric gas-ionic reaction spectra of the alkali metals.

---

<sup>o</sup> *Scientific Papers*, No. 456.



Data are given showing that increasing the atomic weight of the acid element in the salts of thallium shifts the maximum of the spectrophotoelectrical reaction towards the long wave-lengths. The maximum of the spectrophotoelectrical sensitivity of Tl Cl is at  $0.365\mu$ ; of Tl Br at  $0.413\mu$ ; and of Tl I, at  $0.455\mu$ .

The photoelectrical sensitivity curves of the halide salts of thallium have the outline of what appears to be the typical spectrophotoelectrical reaction curve, *viz.*, a high photoelectrical reaction on the short wave-length side of the maximum, and a very abrupt termination of the reaction on the long wave-length side of the maximum.

Lowering the temperature of Tl I to  $-60^{\circ}\text{C}$ . had no appreciable effect upon the position of the maximum of the spectrophotoelectrical reaction.

Of the halide salts of lead, Pb Cl<sub>2</sub>, Pb Br<sub>2</sub>, and Pb I<sub>2</sub>, only the iodide was found to react photoelectrically. The spectrophotoelectrical sensitivity curve of lead iodide appears to be complex with an ill-defined maximum in the region of  $0.45\mu$ , and sharply defined maximum at  $0.52\mu$ .

The halide salts of silver appear to be sensitive photoelectrically when melted into a vitreous or semi-vitreous mass. Silver chloride exhibited photoelectrical sensitivity in the region of  $0.38\mu$ . Silver bromide has a maximum at  $0.46\mu$ . The sensitivity curve of silver iodide appears to be wide and complex with maxima at about  $0.47\mu$  and  $0.50\mu$  respectively.

In connection with these silver halide salts, an examination of samples of silver nitrate and potassium nitrate showed no photoelectrical sensitivity.

---

**GASES IN METALS: I. THE DETERMINATION OF COMBINED NITROGEN IN IRON AND STEEL AND THE CHANGE IN FORM OF NITROGEN BY HEAT TREATMENT.<sup>†</sup>**

By Louis Jordan and F. E. Swindells.

[ABSTRACT.]

THE only form of nitrogen determined in iron or steel by the Allen or acid-solution method is that present as combined nitrogen, probably existing as nitrides of iron, or of such minor constituents as manganese, or aluminum. The solution of the metal sample for nitrogen analysis is made in hydrochloric acid of sp. gr. 1.11.

---

<sup>†</sup> *Scientific Papers*, No. 457.



This solution may be carried out in a covered beaker heated on a steam bath. If solution is hastened by heating over a free flame, or on a hot plate or sand bath, ammonia is lost and low values for nitrogen result. The distillation of this solution for ammonia is best made with condensers having block tin inner tubes. Such condensers give blanks equivalent to 0.000015 g-nitrogen with the same reagents which give blanks of 0.0001 to 0.0002 g-nitrogen with glass condensers. The ammoniacal distillate is collected in 0.01 normal sulphuric acid and the excess acid titrated with 0.01 normal sodium hydroxide, using sodium alizarine sulphonate as an indicator. Estimation of the ammonia in the distillate by means of Nessler's solution gives results too low with steels containing more than 0.1 or 0.2 per cent. carbon.

It has been found that heat treatment of certain steels increased the amount of nitrogen as determined by the Allen method. Such increases have been found in an electric furnace silico-manganese spring steel, in a plain carbon steel from the outside surface of an autoclave plate, and in a series of electrolytic iron ingots. This increase did not take place in an open hearth silico-manganese steel of the same composition as the electric steel, in the plain carbon steel from the inner surface of the same autoclave plate, nor in a second series of electrolytic iron ingots. It is probable that this increase in combined nitrogen is the result of the conversion of uncombined nitrogen to nitride nitrogen by heat treatment, and that nitrogen in two forms was present originally in those samples in which the increase took place.

---

#### APPARATUS FOR THE DETERMINATION OF THE MAGNETIC PROPERTIES OF SHORT BARS.<sup>s</sup>

By M. F. Fischer.

[ABSTRACT.]

IN many cases it is desirable to determine the magnetic properties of materials which are available only in small quantities, such as pure alloys, alloys of experimental composition, and the like. For the correlation of the magnetic properties with various factors such as composition and heat treatment, it would be a distinct advantage if only small samples were required. The ordinary methods of magnetic testing, however, require relatively large

---

<sup>s</sup> *Scientific Papers*, No. 458.



samples, so that a method for the testing of small samples with satisfactory accuracy and speed would greatly facilitate such work. In order to meet this need an apparatus has been developed which is capable of testing such samples with a degree of accuracy sufficient for most purposes.

The method involves the comparison of the unknown sample with one whose properties have been previously determined. Because of the principle involved the apparatus is referred to as a comparator and was constructed especially to measure samples 6 mm. in diameter and of a minimum length of 10 cm.

The apparatus consists primarily of an electromagnet with yoke and pole pieces of Norway iron and with a magnetizing solenoid surrounding the yoke. Symmetrically located in the ends of the poles are two 6-mm. holes with centres 12 mm. apart in which the known bar and the bar to be tested are lightly clamped by means of thumb screws. Coaxial with these holes and held in position between the poles are two test coils of 100 turns each wound on brass forms surrounding the two bars. Each of these test coils can be separately connected to a ballistic galvanometer through the secondary of a calibrating mutual inductance.

Values of induction are measured by means of a ballistic galvanometer connected to the test coil surrounding the test bar. Values of magnetizing force are obtained by noting the inductions in the second bar, called the reference bar, and from a suitable calibration curve determining the magnetizing forces corresponding to the observed inductions.

If the two specimens were subjected to the same value of magnetizing current, the inductions in the two bars would be proportional to their respective permeabilities, and the induction in the reference bar under such circumstances could be used to directly indicate the magnetizing force. Such a simple procedure is not possible, however, as the reluctance of the joints and leakage from the bars cause discrepancies which are too large to neglect. This source of error has been overcome to a large extent, by calibrating the apparatus with standard bars of various properties which have been previously determined by a standard method.

By the use of a suitable series of calibration curves whose coördinates are the inductions in the reference bar and the corresponding values of magnetizing force as obtained from the standard bars the apparatus is capable of yielding satisfactory results.



If an unknown bar is substituted for the standard and corresponding values of induction for the unknown and reference bars are determined, these calibration curves can be used for determining the values of magnetizing force.

Values of residual induction are obtained by noting the change in induction when the magnetizing force is reduced to zero from some specified maximum.

The determination of coercive force requires the calibration of a second reference bar. This is also done by means of several standard bars whose coercive forces have been obtained by the standard method. With the reference bar and one of the standard bars in the comparator, the induction is set at the value from which coercive force is to be obtained, usually the induction corresponding to a magnetizing force of 150 gilberts per cm. The application of the coercive force of the standard bar will reduce the induction in that bar to zero and will at the same time reduce the induction in the reference bar to some other value. This value of induction and the corresponding demagnetizing force are the coördinates of a point on the calibration curve. Other points are obtained with standard bars of different coercive forces. This curve is used in subsequent testing to indicate value of coercive force and is used in a manner similar to that by which it was obtained.

This apparatus is not sensitive to external influences and is capable of producing results which, in general, are in error by less than 5 per cent. of the magnetizing force corresponding to a given induction. For certain types of material, errors greater than this may occur for low values of induction, but in any case the accuracy is determined by the degree to which the properties of the standard bar used in the determination of the calibration curve approximate those of the bar under test.

---

#### SPHERICAL ABERRATION IN THIN LENSES.<sup>9</sup>

By T. Townsend Smith.

[ABSTRACT.]

THIS paper presents an elementary theory of the spherical aberration of thin lenses, to give means for determining quickly the aberration of any thin lens for any position of the object,

---

<sup>9</sup> *Scientific Papers*, No. 461.



and to formulate a statement of the conditions under which the spherical aberrations of two thin lenses will compensate one another. This last is confined to the simplest case, in which the lenses are close together. The treatment is in part analytical, in part graphical.

In addition, there is included in this paper a graphical solution of the problem as to the conditions under which a two-piece lens may be achromatic, free from axial spherical aberration, cemented, and free from coma, and the shapes of the lenses necessary to satisfy these different conditions are shown. The effect of a slight change in the shape of the lenses is also indicated.

It is not expected that any of the material is really new, but the author knows of no place where the information given may be readily obtained, even piecemeal.

---

THE PREPARATION AND PROPERTIES OF PURE IRON  
ALLOYS: II. MAGNETIC PROPERTIES OF IRON-CARBON  
ALLOYS AS AFFECTED BY HEAT TREATMENT AND  
CARBON CONTENT.<sup>10</sup>

By W. L. Cheney.

[ABSTRACT.]

THIS paper discusses effects of heat treatment and chemical composition on the magnetic properties of a series of unusually pure iron-carbon alloys ranging from pure iron to 1.6 per cent. carbon. The alloys were prepared from deposited pure iron (obtained electrolytically) together with a regulated amount of carbon melted in a vacuum furnace.

The test specimens in the form of rods were given the following heat treatments: (1) Two sets of specimens (*i.e.*, two rods from each percentage of carbon) were hardened by quenching in oil and water from suitable temperatures. After the quenching, the specimens were accurately ground to a uniform diameter of 6 mm. and were drawn back to successively higher temperatures (alternating for the two sets) by heating in a suitable bath and allowing to cool slowly in lime.

Another set of specimens was annealed by slowly heating to a desired temperature in an evacuated electric furnace and allowing them to cool very slowly.

---

<sup>10</sup> *Scientific Papers*, No. 463.



After each heat treatment, measurements were made of the normal induction for magnetizing forces up to 2500 cgs. units, and of the residual induction and coercive force from maximum magnetizing forces of 100, 200 and 1000 cgs. units. Other magnetic quantities could be calculated from the observed values.

Micrographs, all at a magnification of 500 diameters, represent the average structural condition shown by etching in a 5 per cent. alcoholic picric acid. Such micrographs were made of the quenched specimens, those drawn back to 270° C., those drawn to 700° C., and the annealed specimens.

The results of the investigation may be summarized as follows:

1. The hardened alloys when drawn back to successively higher temperatures show certain magnetic transformations: (a) A rapid rise in the induction ( $H$  constant) between 200° and 250° C., finally reaching a maximum at some definite temperature and gradually decreasing. (b) A similar trend of the residual induction but less rapid rise, with a delayed maximum and a somewhat more rapid descent following. (c) Marked changes in the coercive force; the greatest decrease being between 200° C. and 300° C. A cusp in the curve occurs in the neighborhood of 470° C., indicating a structural change of the material at this temperature. (d) Similar changes are shown by considering the product  $B_m \times H_c$ , which is proportional to the dissipation of energy owing to hysteresis. (e) The reluctivity relationship is employed to compute the saturation intensity of magnetization. In some cases this maximum value of the intensity was single valued, in some cases double valued, and in only a few cases triple valued. Micrographs confirmed in the majority of cases the fact that the number of values of  $I_m$  represents the number of constituents present in the material. (f) The intercept value of the reluctivity line also serves to detect transformations and to indicate the presence of more than one constituent. (g) Values of the maximum permeability show very great differences for certain alloys as compared with small differences in other magnetic quantities.

2. For the annealed alloys: (a) Magnetization curves (for low inductions) show a decided change in the steepness of the curve in the second stage and hence a change in the permeability, with a change in the percentage of carbon content. (b) The



coercive force has a maximum for the highest carbon used. (c) The maximum intensity of magnetization which was double valued except for pure iron where it was single valued, and for 1.55 per cent. carbon where it was triple valued, decreased with an increase in the carbon content. (d) Micrographs confirmed the number of constituents which might be predicted from the number of values of  $I_m$  in all cases except the 1.55 per cent. carbon.

3. The experiments bring out the following points: (a) The sensitiveness of magnetic quantities to any slight changes of metallographic structure as a result of heat treatment. (b) The necessity of very accurate control in heat treating specimens for a study of their magnetic properties. (c) No definite quantitative relationship can be established between the various magnetic quantities and the heat treatment, or between the various magnetic quantities and the chemical composition. (d) All magnetic quantities must be considered in studying the effect of heat treatment and chemical composition.

---

## VARIOUS PHOTOELECTRICAL INVESTIGATIONS.<sup>11</sup>

By W. W. Coblentz.

[ABSTRACT.]

THE purpose of this paper is to give miscellaneous data which were obtained in connection with the general investigation of photoelectrical sensitivity, but not heretofore published.

Data are given on the preparation and testing of various sulphides of molybdenum,  $\text{MoS}_2$ ,  $\text{MoS}_3$ , etc., the object in view being the artificial production of molybdenite  $\text{MoS}_2$ , which is photoelectrically sensitive.

The results thus far obtained show that all the wet and dry process preparations of  $\text{MoS}_2$  are photoelectrically sensitive, but the intrinsic sensitivity is far less than that of the photosensitive spots found in some samples of the natural mineral.

From the data at hand it appears that this photoelectrical sensitivity is inherent in the  $\text{MoS}_2$ .

Spectroscopic and qualitative chemical analysis shows no marked difference in the constituents of samples of molybde-

---

<sup>11</sup> *Scientific Papers*, No. 462.



nite, excepting a larger iron content in the material having a high photoelectrical sensitivity.

A number of samples of molybdenite were subjected to heat treatment (1) by passing electrical current through them and (2) by heating them, in some cases under high pressure, in an oven.

The conclusion to be drawn from these tests is that slow heat treatment has no marked permanent effect upon the intrinsic photoelectrical sensitivity in the temperature range up to  $500^{\circ}$  C. At a temperature of about  $600^{\circ}$  C. the sensitivity appears to be permanently decreased. Raising the temperature to a low red (about  $700^{\circ}$  C.) heat destroyed the photosensitivity.

In the heat treatment of stibnite it was found that, aside from a possible shift of the maximum towards the long wavelengths, the spectrophotoelectrical sensitivity curve of the melted and slowly recrystallized material is practically the same as that of the average curve of the native mineral.

Samples of molybdenite and stibnite were subjected to electrical treatment which consisted in passing an alternating current through them for certain intervals of time and then noting the effect upon the photoelectrical sensitivity. The conclusion to be drawn from these experiments is that an alternating current has no marked permanent effect upon the photoelectrical sensitivity of molybdenite and stibnite.

Among the miscellaneous artificial preparations examined for photoelectrical sensitivity were: molybdenum oxide; various sulphides of tin, tungsten, and uranium; also  $\text{Bi}_2\text{Te}_3$  and  $\text{MoSe}_3$ . None of these preparations showed a marked photoelectrical sensitivity.

Data are given on the negative spectrophotoelectrical reaction in molybdenite, confirming and extending previous observations.

A sample of molybdenite was found which has a uniform sensitivity over a wide range of the visible spectrum, and a photoelectrical reaction which is proportional to the intensity of the radiation stimulus. This lends encouragement to the efforts which should be made to produce for radiometers a photoelectrical material, which will have these properties.

From a special examination of these two minerals it appears that molybdenite and stibnite have no sharp bands of photo-



electrical sensitivity in the extreme ultra-violet, but that the reaction gradually decreases with decrease in wave-length.

Several spectral response curves are given of Case's barium and strontium photoelectric cells, which have maxima at  $0.42\mu$  and  $0.39\mu$  respectively. By covering the barium cell with a suitable screen, a spectral response curve is obtained which coincides closely with the visual response of the average eye.

Data are given on the spectrophotoelectrical reaction of cuprous oxide; also of a lead antimony sulphide  $Pb_3SbS_3$ , which shows that the spectrophotoelectrical reaction spectrum of a compound is not the composite of the reactions of the constituents which may be photoelectrically sensitive.

Iodine was found to be photoelectrically sensitive with a maximum in the region of  $0.53\mu$  to  $0.55\mu$ .

---

### PREPARATION AND PROPERTIES OF PURE IRON ALLOYS: III. THE EFFECT OF MANGANESE ON THE STRUCTURE OF ALLOYS OF THE IRON-CARBON SYSTEM.<sup>12</sup>

By Henry S. Rawdon and Frederick Sillers, Jr.

[ABSTRACT.]

MANGANESE is one of the essential materials in the manufacture of steel. In addition to its function as a deoxidizing and a "desulphurizing" agent for steel, it is also valuable for conferring certain desired mechanical properties upon the material, such as high tensile strength. A recent investigation of the Bureau of Standards is concerned with this latter phase of the functions of manganese in steel.

By means of an extensive series of alloys of iron-carbon and manganese with carbon varying from 0 to 1.6 and manganese, 0 to 2 per cent., prepared from pure materials, the effect of manganese on the structures, and hence on the properties, was determined.

The effect of manganese, as observed in annealed alloys, is to confer upon the pearlite a very fine grained or sorbitic structure, even after slow cooling. The relative amount of pearlite present is considerably greater in the alloys of high manganese content than in corresponding ones low in this element. A pronounced increase in Brinell hardness of the annealed alloys accom-

---

<sup>12</sup> *Scientific Papers*, No. 464.



panies the change in structure produced by the addition of manganese. The addition of manganese causes a shift in the eutectoid ratio toward lower carbon content. One per cent. of manganese lowers it to approximately 0.78 per cent. carbon.

In the normalized alloys a pronounced decrease in grain-size was found in those of higher manganese contents, in addition to the structural effects mentioned above. In the annealed specimens no noticeable differences in grain-size were detected for high and low manganese content in alloys of any given carbon content.

The well-known effect of manganese in lowering the transformation temperatures of the materials will account in part for the observed structural changes. It appears also that manganese renders steel more "sluggish" and less responsive to structural changes than many of the other elements which produce a similar lowering of the critical temperatures. While the results of the structural examination will not warrant any definite conclusions concerning the use of manganese as a strengthening element in steel, the results obtained strongly support previous recommendations which have been made by different metallurgists concerning the advantages to be gained from the use of higher manganese, particularly in low and medium carbon steels.

---

## RECLAMATION OF USED PETROLEUM LUBRICATING OILS.<sup>13</sup>

By Winslow H. Herschel and A. H. Anderson.

[ABSTRACT.]

As a measure of conservation of an irreplaceable natural resource it is desirable that oils which are dirty or otherwise unfit for further use should be purified or reclaimed. Automobile oils are subjected to severe conditions of service, and may be taken as an example to illustrate the deterioration of oils in use. Aided perhaps by the catalytic action of metal parts and metal particles worn from the bearings, the heat causes the oils to oxidize in use, with the formation of oxidation products of an asphaltic or tarry nature and an increase in organic acidity. The heavy ends of the fuel, similar in nature to kerosene, leak past the piston rings and work their way down into the oil in the crank case, causing what is known as crank case dilution.

---

<sup>13</sup> *Technologic Papers*, No. 223.



To bring the oil back to its original condition, it is evidently necessary to distil off the heavy ends of the fuel, conveniently by heating with steam. As the heating continues and the kerosene is driven off, samples are taken from time to time and tested for flash point. The increasing values obtained in this test indicate the progress being made. It is also necessary to remove the sediment, consisting of oxidation products, road dust, and metallic particles, and this may be accomplished by filtering or by precipitation, using sal soda as a coagulant.

In tests with an apparatus for reclaiming oil by use of a coagulant it was found that the reclaimed oils would pass the usually accepted tests such as viscosity, flash point, and sediment, although the flash point will be slightly lowered. The tests were not conclusive as regards the efficiency of the process in reducing organic acidity since the oils had not been long enough in use to become very acid. The necessity of reducing the acidity to a very low value is open to question, since there appears to be no danger that the acidity would ever become high enough to cause corrosion, except perhaps of lead or zinc. There is evidence, at least as far as Eastern oils are concerned, that the higher the acidity the less the demulsibility or resistance of an oil to emulsification, but investigation of California oils showed that in some cases they had a higher acidity than ever observed for Eastern oils, and yet would pass the test for demulsibility. If, therefore, there is a necessity for testing for organic acids, it must be on the ground that oils high in acidity will not prove durable in use; but this has not been conclusively proved. The difficulty is increased by the possibility that different oils contain different acids, some of which may be more undesirable than others, but which can not be distinguished by simple chemical tests. In fact, the difference in demulsibility of Eastern and California oils of the same organic acidity would indicate that there was a difference in the kind of acid present.

A possible advantage of oils of high acidity is a low coefficient of friction when used in a bearing. It has been found that if a minute quantity of acid from fatty oils is added to mineral oils, the friction, when the oil is used as a lubricant, is considerably reduced, and it is possible that petroleum acids will have the same effect. In many cases it has been found that an oil which showed a low coefficient of friction would also show a low interfacial ten-



sion. On this account an interfacial tension apparatus was used to determine the effect of organic acids upon the friction, but the results were inconclusive, and tests with an oil friction testing machine are planned. If it should prove that high organic acidity is necessary in order that the coefficient of friction may be low, then it may be necessary to compromise between too high a coefficient of friction or too high an acidity, since the latter would indicate the presence of unsaturated compounds and a tendency toward the rapid formation of oxidation products and possibly sludge.

The cause of sludge formation is not clear, but it appears to differ from an emulsion in requiring considerable time for its development. As an oil continues for a long time in use, it accumulates road dust, carbon and other materials in a finely divided state, and the most probable explanation appears to be that sludge is a case of a permanent emulsion due to carbon or dust in a colloidal condition. However this may be, it is evident that all finely divided as well as coarse impurities should be removed from used oils in reclaiming.

What improvements it may be necessary to make in reclaiming processes will depend upon the progress made in selecting or devising a test for durability of an oil in service. The tests at present available for consideration are organic acidity, sulphur content, carbon residue, demulsibility, and Waters carbonization. When it is decided which of these tests are vital, the reclaiming process may be modified, if necessary, so that the reclaimed oils will meet these tests.

---

#### A NEW METHOD FOR DETERMINING THE RATE OF SULPHATION OF STORAGE BATTERY PLATES.<sup>14</sup>

By G. W. Vinal and L. M. Ritchie.

[ABSTRACT.]

THIS paper describes experiments which have been made to develop a speedy and accurate method for measuring the effect of impurities in storage battery electrolyte. In the present paper the fundamental theory of the method and measurements of the rate of sulphation of the plates in the pure acid are given. An extension of the investigation is planned which will include the effect of added impurities following the method here described.

---

<sup>14</sup> *Technologic Papers*, No. 225.



Preliminary experiments in which small cells were "poisoned" by the addition of the various substances to be studied showed that accurate and consistent results were difficult to obtain. Because of the inaccuracies of this method and the time required it was decided to determine the effect of impurities in terms of the rate of the reaction taking place at the plates. This may be accurately determined in a short time by successive weighings of the plates immersed in solutions which are maintained at constant temperature. The plates were suspended in the electrolytes from the arm of a sensitive balance. By this arrangement, it was possible to weigh each plate without exposing it to the air. The jars containing the electrolyte were contained in a thermostat bath of water which could be controlled to within  $0.01^{\circ}$  C. at any desired point within the range  $20$  to  $40^{\circ}$  C. Weighings of the plates were made daily and the results computed as the increase in weight per hour.

The reaction at the negative plate may be both chemical and electrochemical. The measurements show that the former predominated. The rate of sulphation of these plates was determined in solutions saturated and unsaturated with lead sulphate. The rate of sulphation is greater in the latter case. Significant differences were observed between the results obtained in measuring plates made by different manufacturers.

The rate of sulphation of the negative plates increased as the concentration of the electrolyte and the temperature were increased. The rate of sulphation of the positive plates is much less than for the negative plates. It is assumed to be electrochemical in origin. Corrections for the buoyancy of the electrolyte are necessary. It is possible to compute from the electrochemical equivalents the number of ampere-hours of discharge occurring as local action.

The results of these measurements indicate that this is a satisfactory method for measuring the effect of impurities at the negative plates and probably at the positive plates also. It is more difficult to interpret the results obtained at the positive plates. The method is not immediately applicable to the study of such impurities as serve as oxygen carriers, but can be used to determine quantitatively the effect of metallic impurities of other kinds for which accurate data are lacking at present.



TESTING OF BAROMETERS AND ALTIMETERS.<sup>15</sup>

[ABSTRACT.]

BUREAU of Standards Circular No. 46 discusses methods of testing mercurial and aneroid barometers. It first considers the mercurial type. A distinction is made between the instrumental corrections made necessary by mechanical defects and corrections which must be applied to reduce the readings to standard conditions of temperature and gravity. In general, the instrumental corrections of mercurial barometers are combined and the resultant correction is expressed as a single numerical quantity. When the mercurial barometer is to be used where high accuracy is required an additional correction must be applied to allow for residual gas in the tube. This is called the gas correction. Each precision barometer has to be carefully investigated for this effect and an empirical correction curve or table prepared.

Aneroid barometers are next discussed. This type is used to a large extent: (1) For weather observations; (2) for the determination of altitude, either in mountain climbing or where rapid rates of change of pressure are involved as in aviation; (3) in establishing contour lines, and (4) for a great many engineering purposes where extreme accuracy is not required.

Unlike mercurial barometers, aneroid barometers show errors which depend upon the conditions under which the instrument is used. These are discussed below. An aneroid does not have the disadvantage that its corrected reading must be reduced to standard conditions of temperature and gravity, as is the case with mercurial barometers.

The errors of aneroid barometers are classified as transient, secular, and inherent. Transient errors are those due to the aneroid not being in a physically steady state, while secular errors are those due to changes taking place over a long period of time. Both of these classes of errors can be avoided by careful selection of the instrument. The inherent errors, *i.e.*, those due to imperfections of design or construction and to the physical properties of the material used in construction cannot be completely eliminated. Inherent errors are further subdivided under three heads, namely, mechanical, thermal, and elastic errors.

---

<sup>15</sup> Circular, No. 46.



Precautions to minimize the effects of mechanical errors are: First, always to read the aneroid in the position in which it was tested; and, second, to tap the instrument sharply just before reading.

Thermal errors are those due to the expansion of the parts and to the change of the stiffness of the elastic elements of the aneroid (the spring and vacuum chamber) under varying temperature. Aneroids which are marked "compensated" are compensated only for the effect of the changes of temperature on the reading at sea level pressures, and not for the changes of temperature at lower pressures.

The elastic errors are irreversible time effects caused by the imperfect elasticity of the metal of the aneroid vacuum chamber and springs. They may be designated as: Drift, which is the increase of reading when the instrument is held at a constant low pressure for several hours; hysteresis, which is the excess of the reading with increasing pressure over that with decreasing pressure and which is also evidenced by the fact that the reading at any given pressure depends on the previous rate of change of pressure; and after effect, which is the amount by which the pointer fails to come back to the true reading after any complete cycle of pressure change.

In this connection it is noted that during the past few years the Bureau of Standards has constructed aneroid barometers in which all the common errors of ordinary instruments have been practically eliminated. These instruments, although designed for use in aviation, nevertheless involve the same principles as those to be applied in the design of precision engineering aneroids.

The Bureau of Standards methods of testing aneroids are discussed in detail in Circular 46. These tests are conducted for the purpose of determining the magnitude of the errors, so that the proper corrections can be made in the use of the instruments.

Tables of tolerances for aviation, and for engineering and surveying aneroids are given, also the pressure-altitude table which is used in the United States in calibrating altimeters.

Instructions for applying for tests at the Bureau of Standards and the schedule of fees for the various tests are included.



## BIBLIOGRAPHY OF SCIENTIFIC LITERATURE RELATING TO HELIUM.<sup>16</sup>

THE first edition of the Bibliography of Scientific Literature relating to helium has been revised, and references to the literature published during the years 1919-1921 have been added.

As in the first edition, the titles are grouped under numerous headings and so arranged under each heading that related articles will appear together in their chronological order. Approximately 600 references are given of which about one-third have been added since the first edition.

---

## DESCRIPTION AND OPERATION OF AN ELECTRON TUBE DETECTOR UNIT FOR RADIO RECEPTION.<sup>17</sup>

[ABSTRACT.]

THE apparatus now in use for radio reception, except the most simple types, uses electron tubes. This circular is one of a series of circulars on the construction of simple receiving sets. Bureau of Standards Circulars Nos. 120 and 121 were the first two of this series. Very simple receiving sets such as those described in Circulars Nos. 120 and 121 may use a crystal detector instead of an electron tube. For a description of the electron tube and the principles of its operation reference may be made to "The Principles Underlying Radio Communication," Signal Corps Radio Communication Pamphlet No. 40.

Electron tubes are used for reception in many different kinds of circuits. One of the most elementary is as a simple detector. It is also possible to use electron tubes in reception in circuits using various kinds of amplification, or regeneration, heat reception, or other methods. For descriptions of various kinds of tube receiving circuits, reference may be made to the book, "The Principles Underlying Radio Communication," or to one of various other books now available, of which a list may be found in Bureau of Standards Circular No. 122 (price, 5 cents). A simple tube detector set will not serve to receive signals transmitted by continuous wave radio telegraphy.

This circular describes a simple electron tube detector receiving set and gives a method of operating it. This set with electron

---

<sup>16</sup> Circular, No. 81.

<sup>17</sup> Circular, No. 133.



tube detector is more sensitive than a set employing a crystal detector, and may be expected to give more satisfactory results.

An antenna, lightning switch, ground connection and telephone receivers, which are used in this set, have been described in Bureau of Standards Circular No. 120. Tuning devices for use with this electron tube detector set may be the tuning coil described in Circular No. 120, or the two-circuit coupler and variable air condenser described in Circular No. 121. While the two-circuit tuner will be somewhat more selective than the single-circuit tuner, as stated in Circular No. 121, its use is not absolutely essential. The more selective receiving set can be used for picking out a signal which it is desired to receive from among a number of signals of approximately the same wave-length which are being transmitted at the same time. The two-circuit tuner is somewhat more difficult to operate than the single-circuit tuner.

For an electron tube detector unit, it is necessary to have an electron tube, socket for the tube, filament rheostat, grid leak, grid condenser, by-pass condenser, binding posts, and other minor accessories. It is also necessary to have a 6-volt storage battery, and a "B" dry battery of  $22\frac{1}{2}$  to 45 volts. Most of these parts should be purchased, although some can be made at home if desired. The cost of the complete electron tube detector unit, including the tube and batteries, may be expected to be from \$23 to \$37. This estimate is exclusive of the cost of tuning device and telephone receivers described in Bureau of Standards Circulars Nos. 120 and 121, which may be from about \$10 to \$20. No estimate is made of the cost of equipment for charging storage batteries.

The electron tube, socket, condensers, filament rheostat, grid leak and other parts of the detector unit are mounted on a wooden base and panel. The wood for the base and panel should be thoroughly dry and should preferably be protected by a coat of good electrical insulating varnish.

A complete description of the method of assembling and wiring the detector unit is given. Illustrations are given showing the arrangement of the various parts and the complete assembled detector unit. The method of operating the set is also given.



UNITED STATES GOVERNMENT SPECIFICATION FOR FIRE  
EXTINGUISHING LIQUID (CARBON  
TETRACHLORIDE BASE).<sup>18</sup>

[ABSTRACT.]

FEDERAL SPECIFICATIONS BOARD STANDARD SPECIFICATION NO. 36.

THIS specification was prepared by a technical committee of the Federal Specifications Board and before final approval was submitted to the Underwriters' Laboratories and to a large number of manufacturers of such products, whose suggestions were carefully considered. The specification was promulgated as a Government Standard by the Federal Specifications Board on July 3, 1922, and gives the general requirements and detailed methods of sampling and testing. The general requirements are:

The liquid shall be capable of extinguishing fires caused by the burning of inflammable liquids and solids, shall be a non-conductor of electricity, and shall consist of carbon tetrachloride containing other suitable products necessary to produce a liquid conforming to the following requirements when tested according to the methods herein stated:

(1) *Appearance*.—It shall be a clear, homogeneous, mobile liquid.

(2) *Specific Gravity*.—The specific gravity at 15.5°/15.5° C. shall not be less than 1.500.

(3) *Cold Test*.—The liquid must have a cold test not higher than minus 45.5° C. (minus 50° F.).

(4) *Distillation*.—Not over 2 per cent. shall distil below 60° C. At least 90 per cent. shall distil between 70° and 80° C. At least 99 per cent. shall distil below 100° C.

(5) *Impurities*.—The liquid shall be free from nitrobenzene, water, acid or alkali, and free halogens, and shall not contain more than 1.0 per cent. by weight of carbon disulphide. It shall not corrode metals used in fire extinguishers.

---

CAUSTIC MAGNESIA CEMENT.<sup>19</sup>

[ABSTRACT.]

THE cement resulting from the reaction of caustic magnesia with a solution of magnesium chloride has been known for more than half a century, and some of the products made therefrom.

---

<sup>18</sup> Circular, No. 134.

<sup>19</sup> Circular No. 135.



in the form of resilient flooring, stucco, and ship decking, have been on the market for considerably more than half that period. However, on account of the almost universal practice of hiding the nature of the products under various proprietary trade names, the public has been kept from realizing the wide use and the general qualities of the product.

Caustic magnesia results from burning magnesite at a temperature of  $800^{\circ}$  to  $1100^{\circ}$  C. In this country the magnesite used is the amorphous variety and occurs in California or is imported from Greece or India. After calcination the material is ground and then mixed with the required aggregates to produce any of the products desired. Unlike Portland cement, the general public does not come into contact with the cement itself, but only with the mixture of cement and aggregates which are mixed with the chloride solution after delivery to the job.

References are given to the discovery and early history of this cement. A summary of the investigative work dealing with the process and products of setting is also presented. None of these has satisfactorily explained these phenomena, and conclusive research work remains to be done.

The paper gives certain typical formulas for making flooring and stucco. These are, however, only "typical" and may with the magnesia available in any case, or with the available aggregates, produce very unsatisfactory results unless materially modified. These formulas should first be tried by making test panels and noting shrinkage, expansion, or warpage, and test pieces to determine tensile or transverse strength. The deportment of these test specimens will indicate what modification of the formulas is required. The same test procedure should be followed with each new shipment of caustic magnesia or constituent aggregates. This is necessitated by the readiness with which the properties of the oxide are modified by storage and by small amounts of impurities in the aggregate, or by improper grading of the latter.

On account of the need for testing, certain test requirements and methods for conducting these are given. These are not presented in the form of specifications and methods of tests at the present time on account of the need of further study, but will serve as an outline for those desiring to know more of the caustic magnesia they are using.



**SPECIFICATIONS FOR NUMBERED COTTON DUCK FOR  
GOVERNMENT AND COMMERCIAL USE.<sup>20</sup>**

[ABSTRACT.]

THESE specifications were prepared by a committee of manufacturers appointed by the Cotton Duck Association and representatives of the Bureau of Standards, War Department, Navy Department, Panama Canal, and other Government departments. Each manufacturer supplied his complete range of weights and constructions of both medium and hard texture ducks for laboratory tests on the physical measurements and performances for determination of fair tolerances and requirements.

On final acceptance, it was decided that inasmuch as these specifications were fair and called for a high grade of material, especially in the care and quality of manufacture, it would be to the advantage of the consumer and manufacturer to use these specifications in obtaining a cheaper product by reason of wide acceptance and quality, taking steps to have the Government use the specifications and eventually to have the commercial user accept them. Recommendation for acceptance has been made by the Textile Technical Committee of the Federal Specifications Board.

There are embodied in these specifications two very important developments in the nature of standards of measurements. The manner of expressing the weight per unit area has been changed tentatively from the 22-inch basis to the 36-inch or square-yard basis. Both are recorded in these specifications as it is realized that the change must come gradually. This attempt to standardize on the square-yard basis will include all types of duck, among which are awning duck. A conference in regard to the latter material was held by the Cotton Duck Association and the National Association of Tent and Awning Manufacturers in an effort to substitute the square-yard basis for the 29-inch basis which the latter association was attempting to establish through state and federal legislation in order to do away with the present misunderstanding.

The second development is the establishment of a standard method of testing the breaking strength of ducks. The results of tests by the various methods used were studied, resulting in

---

<sup>20</sup> Circular, No. 136.



the selection of the 1-inch and 1 by 3-inch grab method. The Textile Technical Committee of the Federal Specifications Board has planned to recommend this method only in all specifications for duck, and the American Society for Testing Materials has been asked to consider this method as a replacement of their recommended 1-inch-strip method for tire ducks.

In these specifications, the requirements are such that no changes will be necessary in any one mill, as the minimum thread count allows a manufacturer to exceed in this regard to conform to his equipment, while the breaking strength is sufficiently high to guarantee a good quality of duck. This item was especially called for by the manufacturers' committee in their desire to raise the standard of the trade.

The material will be purchased by expressing the following:

(a) Number of duck or weight per square yard; (b) texture (medium or hard); (c) width; (d) yardage; (e) use; (f) statement as to whether or not material is to conform to standard specification.

---

**Study of the Spectrum of the Light Emitted in the Triboluminescence of Sugar.** H. LONGCHAMBRON. (*Comptes Rendus*, June 19, 1922.)—When lumps of sugar are broken flashes of light appear. A few observations made on this light have seemed to indicate that the spectrum is continuous. Such is not the conclusion to which the present paper comes. The sugar was broken in air at atmospheric pressure in front of the slit of a spectrograph for a period of more than four hours. The integrated impression of the several flashes on the plate showed a series of 23 bands very narrow and well separated. These correspond to most of the bands of the second positive band spectrum of nitrogen and to no other spectrum. It is the spectrum of the electric glow in air. Air charged with sugar powder made by breaking up lumps has an electric charge, as is shown by its discharging a charged electroscope over which it is made to flow. Perhaps the flash occurring at the moment of fracture arises in this way. The two resulting fragments may have opposite electrical charges. As they are separated a glow discharge forms between them, which, of course, has the same spectrum as the glow otherwise produced. This explanation is supported by the following experiment: Lumps of sugar were placed in a glass vessel and were shaken against the walls in order to break them. When the air pressure in the vessel was from 4 to .1 cm. of mercury, the light of triboluminescence was more intense than at atmospheric pressure and occupied a much larger space around the point of rupture.



This light at lower pressures was, however, fainter than at atmospheric pressure.

After the shaking of the sugar the walls became covered with the resulting powder. When, then, the air pressure within was rapidly varied, though in all cases maintained rather low, the entire mass of enclosed air glowed brightly, especially near the bits of sugar and the parts of the walls covered with dust. G. F. S.

**A New Method of Power Transmission.**—Considerable literature has recently appeared concerning a new method of power transmission, invented by Constantinesco. It depends on the propagation of waves of condensation and rarefaction through liquids, water, being, of course, the most available. The liquid does not flow in the pipe. A paper by Walter Haddon gives a large amount of detail of the apparatus to be used, and a recent communication to the North-east Coast Institution of Engineers and Shipbuilders presented some of the mathematical and physical features of the subject. Five methods of power transmission have been long in use: Steam, direct mechanical power, electric, compressed air and hydraulic. The new method is, therefore, considered as a sixth one and is claimed to have very important advantages. At first it may be thought that wave transmission is merely a form of hydraulic action, but there is a wide difference. In hydraulic transmission there is a flow of liquid, but in wave transmission the liquid does not flow. The principle may be illustrated by assuming two cylinders each with a plunger and connected by pipe, the whole apparatus being completely filled with water. If one plunger is moved rapidly up and down it will set up waves of compression at each downward stroke, which will travel through the water at a speed stated to be about 4800 feet per second, and exert a pressure on the other plunger. If the distant plunger is loaded, a reciprocating motion can be established as long as power continues to be applied to the first apparatus. It is claimed that the principle has been brought to practical application, with the advantages of: Simplicity, adaptability, portability, low initial cost and low maintenance charges. A condition of satisfactory operation is that the whole apparatus shall be filled with liquid to the complete exclusion of air, which is secured by special appliances. Wave transmission can produce rotary motion by single phase (one liquid column) or by three phase (three column). The method was first applied to rock drills, riveters, and pile drivers, in which reciprocating motion is employed. By a modification the water can be allowed to flow out, and thus a dustless rock drill has been devised. It is claimed that in a properly constructed line, no appreciable rise of temperature occurs. In some cases oil may be used as the transmitting liquid. Pamphlets describing the methods, apparatus and many possible applications have been issued. H. L.



## NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.\*

### NOTE ON THE ENERGY EXCHANGES IN THE FORMATION OF THE LATENT IMAGE OF A PHOTOGRAPHIC EMULSION.<sup>1</sup>

By S. E. Sheppard and E. P. Wightman.

THE authors present a recalculation of some energy calculations by Volmer showing the number of molecules per grain affected by the "schwollenwert" (visible threshold value) exposure and of the ratio of altered to unaltered molecules in a grain of the size assumed. Evaluation of the possible energy changes considered here are to be presented in a future paper.

### ELASTICITY OF PURIFIED GELATIN JELLIES AS A FUNCTION OF HYDROGEN ION CONCENTRATION.<sup>2</sup>

By S. E. Sheppard, S. S. Sweet, and A. J. Benedict.

INVESTIGATION has been made of the relation of the jelly strength (modulus of rigidity) of purified gelatin jellies at different gelatin concentrations and over a wide range of hydrogen ion concentrations. The gelatin was demineralized and freed from products of hydrolysis by successive electrolysis and precipitation with acetone. The hydrogen ion concentration is expressed as the Sorensen value  $P_H$ , and it was found that the maximum jelly strength is produced between  $P_H = 7$  and  $P_H = 9$ . No definite minimum was observed at the isoelectric point 4.7-4.8, but the curve has a slight shoulder in this region after which for  $P_H < 4$ , the jelly strength falls off very rapidly, as it does also for  $P_H > 10$ . It was found, further, that amounts of aluminum, equivalent to only 0.01 to 0.1 per cent. of alumina, based on dry gelatin, produced very considerable changes in the jelly strength- $P_H$  curve. The total jelly strength was greatly increased, and a new maximum was developed at about  $P_H = 4.0$ . These results are discussed in connection with the theory of gelatin viscosity and elasticity. A misleading statement on Poisson's ratio (for gelatin jellies) in a previous paper, and in the literature of the subject, is corrected.

---

\* Communicated by the Director.

<sup>1</sup> Communication No. 151 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, Nov., 1922, p. 913.

<sup>2</sup> Communication No. 132 from the Research Laboratory, Eastman Kodak Company, and published in *J. Amer. Chem. Soc.*, Sept., 1922, p. 1857.



## THE GRAININESS OF PHOTOGRAPHIC MATERIALS USED IN THE MOTION PICTURE INDUSTRY.<sup>3</sup>

By A. C. Hardy and Loyd A. Jones.

AN instrument used for measuring the graininess of silver deposits in photographic materials is described. The essential principle involved is the determination of the distance at which the graininess of the deposit under consideration, which has been magnified to a definite predetermined extent, is just invisible. It is shown by the aid of photomicrographs that the readings obtained by this instrument represent the graininess of the material as this term is understood by the photographer. The influence of various steps in the preparation of the motion picture positive upon the graininess of the resultant picture has been determined.

It was found that a negative exposure in the taking camera had marked influence on the graininess of the resulting positive print, the minimum graininess being obtained by a minimum exposure.

The time of development of the negative had very little influence on the graininess of the resulting print when a constant positive quality was maintained.

Dilution of a developing solution in general produced a slight increase in graininess.

Graininess was found to be almost entirely independent of the developing agent used for the development of a negative.

Fixing, washing, and drying conditions were found to have very little effect on graininess.

Prints made by ultra-violet light showed a measurable degree of graininess. This was also found to be the case when diffused light was used in making the prints.

An explanation is offered for the excessive graininess which sometimes occurs with certain types of subjects. This is probably due to the nature of the subject which requires the rendering of large unbroken areas by positive densities which lie near the maximum graininess. The various remedies for this condition are discussed.

---

<sup>3</sup> Communication No. 145 from the Research Laboratory of the Eastman Kodak Company, and published in *Trans. Soc. Mot. Pict. Eng.*, No. 14, May, 1922, p. 100.



## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

### EFFICIENCY OF THE PALMER APPARATUS FOR EXPLOSIVE CARBONACEOUS DUSTS.<sup>1</sup>

By L. J. Trostel.

[ABSTRACT.]

THE efficiency of the Palmer dust sampler was determined, on a weight basis, on heavy suspensions of ten dusts of varying chemical and physical properties, which are explosive hazards in the elevator, milling, and chemical industries. Microphotographs of the various dusts tested were made.

The sampler retained an average of 98.2 per cent. of the dust added to it.

There is no evidence to show that the efficiency is appreciably affected by the varying of the sampling rate from 3 to 5 cubic feet per minute under the conditions of the test.

The efficiency appears to increase with the weight of dust collected, up to certain limits.

The maximum weight possible to collect efficiently ranges from approximately 1.5 grams to 3.0 grams, depending upon the nature of the dust.

The efficiency is higher when dusts of large particle-size are being collected.

### CHEMICAL CHANGES IN CALCIUM ARSENATE DURING STORAGE.<sup>2</sup>

By C. C. McDonnell, C. M. Smith and B. R. Coad.

[ABSTRACT.]

COMMERCIAL calcium arsenate in the dry powdered form manufactured for insecticidal purposes absorbs carbon dioxide slowly from the atmosphere during storage and increases slightly in water-soluble arsenic-oxide content, unless it is packed in containers that are practically air-tight. The rates of these changes show a close relationship and depend largely upon the type of container in which the material is packed.

---

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *J. Am. Soc. Heat.-Vent. Eng.*, 28, Dec., 1922, 853.

<sup>2</sup> Issued as *U. S. Dept. Agr. Bul. 1115*, Nov. 28, 1922.



### A PHYSICAL AND CHEMICAL STUDY OF MILO AND FETERITA KERNELS.<sup>3</sup>

By George L. Bidwell, Leslie E. Bopst and John D. Bowling.

[ABSTRACT.]

ON the whole, kafir, corn, milo and feterita resemble one another in composition and appearance. The proximate constituents of the kernels of these sorghums indicate their value as food for man and domestic animals, and show the possibility of their being used as raw products in certain important commercial operations having for their purpose the manufacture of starch, syrup, alcohol, and oil, when proper machinery and processes have been devised. It has been found, however, that it would probably be impracticable to use them commercially for malting purposes.

---

### SUGGESTIONS FOR THE PREVENTION OF FOOD POISONING.<sup>4</sup>

By Charles Thom.

[ABSTRACT.]

THE following practical summary of the precautions necessary to avoid food poisoning are based on the present status of information on food infections of the enteric group and botulism:

1. Food to be eaten raw should be fresh, clean, sound, and free from stale odors, from slimy, rotting areas, from discolorations, and from mold. It should be carefully washed in an abundance of bacteriologically clean water (that means drinking water).
2. Sound food freshly cooked does not cause food poisoning.
3. Moist or soft cooked food if held for more than a few hours should be kept in a good refrigerator. If such refrigeration is impossible, the food should be recooked before serving.
4. The frequency of enteric outbreaks and of botulism clearly points to a very general failure to appreciate the dangers of bacterially contaminated and spoiled food. Detailed suggestions for inspection of canned food are presented in this paper.
5. Responsibility for eliminating spoiled food from human consumption rests equally upon the packer, the dealer, and the person who prepares it for the table. Every one who handles food should be familiar with standards of quality, appearance, odor, and texture of the product, whether in bulk or in sealed containers.

---

<sup>3</sup> Issued as *U. S. Dept. Agr. Bul. 1129*, Nov. 27, 1922.

<sup>4</sup> Published in *Am. Food J.*, 17, Nov., 1922, 15.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

---

### TECHNOLOGY OF SLATE.

By Oliver Bowles.

THE writer recently completed a careful study of about sixty-five active slate quarries and finishing plants in Pennsylvania and Maine; New York and Vermont; Maryland-Pennsylvania, and Virginia.

The chief products of manufacture are roofing slates, blackboards and school slates, electrical switchboards, billiard tables, shower stalls, steps and various other forms of structural slate. Waste constitutes a very important problem in all slate quarry operations, the proportion of waste varying from 65 to 95 per cent. Much study was devoted to improvements, whereby waste could be partly eliminated, and to determine more extended uses for unavoidable waste. Experiments by industrial laboratories indicated that pulverized waste slate could be used to advantage as a filler in road asphalt mixtures, plastic roofing and flooring, and various other products. Many other uses of slate refuse are discussed. However, due to the difficulty of developing a wide market for waste slate, quarrymen should devote their attention primarily to means of eliminating waste to the greatest possible extent. Further details will be found in Bulletin 218, of the Bureau of Mines.

---

### ROCK STRATA GASES IN MINES OF A NEVADA MINING DISTRICT.

By E. D. Gardner.

IRRESPIRABLE gases issuing from the rock formations are a source of expense and danger in some metal mines. There is a great variation in the composition of such gases and, as shown by recent sampling by the Bureau of Mines, the gas may consist mostly of carbon dioxide ("Rock Strata Gases in the Mines of the East Tintic Mining District," by G. E. McElroy, Bureau of Mines Serial 2275), or of methane ("Methane in California Gold Mines," by B. O. Pickard and E. D. Gardner, Bureau of Mines Serial 2303), or nitrogen, as in the present instance.

---

\* Communicated by the Director.



A number of unventilated raises in some of the mines of a Nevada district contain accumulations of a high-nitrogen gas that will not support life or combustion. The raises are in different geological formations and in widely separated localities in the mining district. One of two raises in the same formation may be full of the gas and another nearby be free of it. Lives have been lost and a number of men have been overcome on entering unventilated raises in which the irrespirable gas had accumulated between shifts. Generally, however, the gas seems to "ooze" from the formation and to accumulate so slowly that its presence is not suspected at the time, but discovered after the raise is abandoned. Occasionally it issues from a newly cut crevice or fissure under considerable pressure and in large enough quantities to overcome or drive out men working in unventilated places. Further details are given in Serial No. 2427 of the Bureau.

---

#### REMOVAL OF SULPHUR FROM GASOLINE.

By D. B. Dow.

THE Bureau of Mines has completed an investigation of the practical operation of gasoline plants in the mid-continent field, in which gasoline containing objectionable sulphur compounds is treated for removal of the sulphur. When the need for such treatment first became obvious about 1920, in order to permit such gasoline to meet rigid export requirements, the Bureau of Mines first developed a suitable method and was largely instrumental in having it installed by the gasoline operators. The report on the present investigation, which deals with the costs and efficiencies of the treatment as applied in the different plants, will soon be available. Data were obtained on construction, accurate operating costs, and photographs of gasoline treating plants at Shidler, Oklahoma, and Kansas City, which are claimed to be the largest plants of their type in the world.

---

#### STUDY OF NEW ALBANY SHALE.

By John R. Reeves.

IN 1921, a section was bored with a core drill by the Louisville Cement Company, through the New Albany, Indiana, oil shale, in Clark County, Indiana. The shale formation was struck at a



depth of 4 feet 11 inches and was found to have a total thickness of 98 feet 5 inches. It was found that the upper 35 feet and the lower 20 feet of the formation are the richest while the lowest yield was obtained from near the middle of the formation. The average yield for the entire formation at the location of this drilling is 8.3 gallons per ton. The average yield for the upper 50 feet is 11.6 gallons. Between 50 and 60 feet, the yield is very low, while from 60 to 98 feet it averages 7.0 gallons per ton. The New Albany formation constitutes the principal oil shale deposit of Indiana and outcrops in the southeastern part of the State, between North Vernon and New Albany. The outcrop district, running north and south, is about 50 miles long and from 5 to 15 miles wide. The same shale also outcrops in the northwestern part of the State, along the banks of the Wabash River and its tributaries in White and Carroll Counties in the vicinity of Monticello, Delphi, and Rockfield. The southeastern or principal outcrop district covers parts of Jennings, Jefferson, Jackson, Scott, Clark and Floyd Counties. This district extends south into Kentucky, the New Albany shale being coterminous with the Devonian oil shale of that State. Further details are given in Serial 2425, Reports of Investigations.

---

**Breakage of Watch-springs.**—S. R. Williams, of Oberlin College, has investigated the cause of the spontaneous breaking of main-springs in watches, a common and annoying incident. It appears that watch repairers are inclined to the view that such breakages are seasonal, occurring principally in the warmer months. Williams was permitted to examine the records over several years of two firms doing a large repair business, and on plotting the results found in both cases a peak in summer fairly coincident with the peak of the graph showing the occurrence of thunder storms. There was, however, in both cases, a slight dip about mid-July, which has been ascribed to the absence of many persons on vacation. Herman Seemann, a pupil in advanced standing in the department of physics at the College, made experiments in the matter, and the results indicate that the breakage is not due to heat but to moisture. Williams thinks that the moisture acts by starting rusting points which weaken the spring at those points. In an experiment, in which fifty-six samples were tried, equally divided between two well-sealed jars, one containing dry and the other moist air, seventeen springs broke in the latter and none in the former. Seemann also found that oiling the spring diminishes very markedly the liability to break. H. L.



**The Effect of the Magnetic Field on the Absorption of X-rays.**  
J. A. BECKER. (*Phys. Rev.*, August, 1922.)—"It was hoped that an applied magnetic field would orient the ultimate magnetic particle and that this shifting would result in a measurable change in the absorption of X-rays. A study of this effect would throw a new light on the nature of the ultimate magnetic particle and on its function in the atom." It was supposed that the result would be small. Hence a sensitive method was devised, correct to a few parts in 100,000. Two beams of X-rays from the same Coolidge tube were admitted into two identical ionization chambers of cylindrical form filled with methyl bromide and connected by a glass tube to insure the existence of the same pressure in both. The casing of one chamber was connected to the positive terminal of a battery while that of the other chamber was joined to the negative terminal. The middle point of the battery was earthed. The entrance of the X-rays into the respective chambers was followed by the ionization of the gas and by a consequent accumulation of charges upon metal rods running along the axes of the cylinders. In one chamber this charge was positive and in the other negative. Both of these rods were joined to the leaf of a Bumstead electroscope. If everything in the path of one beam is exactly equivalent to the corresponding feature in the path of the other, just as much positive electricity will be found on the rod of one chamber as there is negative on the rod of the other and the leaf, joined to both rods, will not be affected. To bring about this state a variable slit was placed in the path of one beam and the beam passing through it was regulated so as to produce a minimum motion of the leaf of the electroscope. This adjustment was made when there was in the path of each beam a specimen of the material to be examined. The specimen in the beam without the slit was between the poles of a powerful electromagnet. Upon the application of the magnetic field the strength of the beam emerging from the specimen in its path was changed. This caused a change in the ionization within the chamber and in the electric charge and, finally, in the motion of the leaf. What is sought is a knowledge of the change in the absorption of the beam by the specimen upon the turning on of the magnetic field. This can be calculated from the change in the aperture of the slit necessary to produce the same motion of the leaf.

The results were not the same when the magnetic lines of force were perpendicular to the beam as when they were parallel to it. In the case of iron both directions of the field cause a decrease in the absorption coefficient for X-rays, while for copper, nickel, aluminum and platinum an increase is produced. With carbon and zinc an increase is caused by one direction of the field and a decrease by the other. The field employed was about 18,000 gauss. Even with this the changes observed in the absorption of rays of wave-length .3 Angström unit were small in all cases.

G. F. S.



# THE FRANKLIN INSTITUTE.

---

*(Proceedings of the Annual Meeting held Wednesday, January 17, 1923.)*

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, January 17, 1923.

DR. WALTON CLARK, President, *in the Chair.*

The Board of Managers submitted its report. The report recorded the elections to membership of:

Charles S. Chrisman, Esq., Engineer, United Gas Improvement Company, 1401 Arch Street, Philadelphia, Pennsylvania;

William H. Kavanaugh, Esq., M.E., Professor of Experimental Engineering, University of Pennsylvania, Philadelphia, Pennsylvania;

Lewis F. Moody, Esq., B.S., M.S., Consulting Engineer, The William Cramp and Sons Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania;

J. H. Mull, Esq., Shipbuilder, President and General Manager, The William Cramp and Sons Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania;

Horace C. Porter, Esq., Ph.D., Consulting Chemical Engineer, Professional Building, 1833 Chestnut Street, Philadelphia, Pennsylvania;

Harvey Birchard Taylor, Esq., Vice-president, The William Cramp and Sons Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania;

a lecture before the Stated Meeting December 20, 1922, by

W. F. G. Swann, D.Sc.,

Professor of Physics,

University of Minnesota,

Minneapolis, Minnesota,

on "Unsolved Problems of Cosmical Physics";

and additions to the library by gift, 116 volumes and 42 pamphlets; by purchase, 12 volumes.

The tellers of the election, Messrs. Jennings, Leffmann and Picolet, reported the ballots cast for President, Vice-president, Treasurer and members of the Board of Managers showed that the following gentlemen were elected to the respective offices indicated:

Walton Clark, President (to serve one year); W. C. L. Eglin, Vice-president (to serve three years); Benjamin Franklin, Treasurer (to serve one year); Managers—Gellert Alleman, G. H. Clamer, Theobald F. Clark, Walton Forstall, Benjamin Franklin, Harry F. Keller, George D. Rosengarten, William Chattin Wetherill (to serve three years); J. T. Wallis (to serve two years); J. Bartleman Klumpp (to serve one year).



The President read the annual report of the Board of Managers for the fiscal year ending September 30, 1922, commenting upon the reports of the various standing committees of the Institute and of the Board of Managers.

He then recalled that the Institute was meeting on the two hundred and seventeenth anniversary of the birthday of Benjamin Franklin and recognized Mr. James S. Rogers, who made the following remarks:

"Mr. President, Ladies and Gentlemen: It would be a pleasure to speak anywhere of Franklin, but particularly so in the presence of members of this Institute bearing his honored name. And it is most appropriate to do so standing before the Sully 'bust' portrait of him hanging on the wall here, and beside our treasured tools of his trade and instruments of his scientific toil—here in this hall where we feel the power of his personality pulsating through the ages, pick it up, amplify it as much as we can, and relay it on to future generations.

"In a few minutes during which the regular order of business may be encroached upon, it would be impossible to mention the great achievements of Franklin. And it would be unnecessary to do so, as you are all familiar with them.

"So I will confine myself to a few things of a general nature, which set out in a broad way his spirit and the influence of his life and works.

"The world, through the ages, in varying degree with different peoples, has largely been dominated by the religious mind. In so far as the religious mind has been of deep, true, spiritual insight, it has been the great light of the world, and the greatest beacon on the pathway of progress. In so far as it has surrendered itself to ignorance, superstition, and bigotry, it has been a hindrance to progress.

"The world has also, particularly in certain countries and at certain times, been greatly lead by the legal mind. In so far as this legal mind, including, of course, the judicial mind, has had broad vision, looking forward as well as backward, it has been one of the greatest influences in social development, probably the greatest influence next to the religious mind, with the possible exception of the mind influence of the noble teaching profession. But in so far as it has too much looked backward to precedent, and delighted in technicalities rather than substance, it has hindered rather than helped.

"And always there has been the influence of the business mind, with the business man trying to square his conduct with both the precepts of religion and the commands of law; and giving valuable object lessons to both the religious and the legal mind in applied religion and ethics in daily life.

"In recent generations there has grown into almost dominating prominence the scientific mind; the mind that inquires before it accepts, that seeks to know, that looks forward more than backward, that builds constructively and works for the betterment of human conditions. It clears away from the religious mind the befogging clouds of mere superstition, and breaks down the barriers of bigotry. It questions the edicts of the legal mind, and bids it free itself from the entanglements of outgrown precedent, that it may see changes which have taken place, and provide accordingly. It supplies the business man with the means of great works. And yet it, too, has its faults, and one word of



caution in lauding it is necessary. It sometimes in conceit at its own accomplishments fails to see, above and beyond, the Divinity which established the cosmic order, and all the little that has been discovered of it.

"It is one of Franklin's greatest services that in the early years of really scientific research he gave a splendid and inspiring example of the spirit, methods and accomplishments of the scientific mind.

"Of this a simple illustration may be taken, for simple illustrations are often most illuminating; and there is one at hand suggested by the tablet you have noticed in the hallway to this room, erected to Franklin by the Stove Manufacturing Industry of the United States, and commemorative of his invention of the Pennsylvanian Fireplace, which in its subsequent portable form has become known as 'The Franklin Stove.'

"In his pamphlet describing this invention Franklin shows forth most interestingly the spirit and methods of the scientific mind

"He begins with an examination of the prior art and existing methods of heating houses. After pointing out their merits and defects he takes up particularly the large open fireplace, with huge chimney, then in general use, burning cord wood. He points out their excessive and wasteful consumption of wood; and that if this is persisted in it will in time unduly deplete the forests and burden later generations with increased cost of wood. In this you will see his foresighted thought for his fellowmen in later years.

"He shows that in such fireplaces a large part of the heat goes to waste up the chimney place; for air when heated rarifies and rises. And as that truth was not so generally known as now, he gives two simple experiments by which, if you doubt it, you can prove it.

"He points out that the air which goes up the chimney must be replaced, and that this brings air whistling in with unpleasant noise through the cracks of doors and windows; but this does not supply enough air and smoke comes out into the room. To furnish enough air and draft, he says it is customary to open doors or windows. That brings in so much cold air that the family draw up close to the fire, frequently without room enough around it for them all, and they roast in front and freeze in back. To overcome this, high-back settles are built.

"He takes up objections which some make to living in heated rooms, alleging that it is unhealthy and subjects one to taking cold upon going out. As opposed to this, he sets forth the wonderful power of the body to accommodate itself to different temperatures; among other illustrations points out to his readers that they sleep in warm feather beds, but jump out in the morning into cold rooms, without ill effects.

"He takes up and answers objections to iron stoves, that when heated they give off noxious and poisonous gases, and offensive odors. He cites the good health of those who work around heated iron, as blacksmiths and workers in iron foundries. He shows that bad odors from iron stoves come not from heated iron, but from untidy housewives permitting the stoves to become covered



with grease and dirt; also that some men are filthy enough to spit on hot stoves to see the sizzle, until such a stench arises in a small room that the nostrils cannot stand it.

"He shows the healthfulness of fresh air, and the advantages of bringing fresh air into the house and heating it to warm the rooms.

"In all of this you will see the careful method of the scientific mind in the observation of facts, and reasoning from observed facts.

"He sets forth with an abundance of illustrative plates, his Pennsylvanian fireplace, with careful instructions for its proper erection.

"In this fireplace he provides an air chamber, against the front of which the fire is built, and of a construction so arranged that the draft draws the flame to the top of the air chamber, across the top and down the back of it, under a false back in the chimney, and then up the chimney. This supplies heat on three surfaces of the air chamber.

"A duct is provided under the floor bringing air from outside the house to the air chamber; and openings in the two opposite ends of this chamber permit the heated air to escape into the room; provision being also suggested for carrying heated air to the room above, if desired. He thus provided in principle a modern hot-air plant, for taking in and heating fresh air.

"Difficulties in getting mechanics to properly erect this most excellent fireplace, gradually led to its abandonment and the substitution of the portable forms of so-called Franklin stoves.

"Another characteristic of Franklin, which may be mentioned in this broad general way, was his devotion to work. From the time when at the early age of ten years he first began to help his father, he worked and toiled for about seventy years of a long and fruitful life. Much of this effort was devoted to constructively bettering the condition of his fellowmen.

"There are many to-day whose remedies for social ills are destructive, and who want others to work in order that they may eat and be clothed and enjoy lazy ease—if lazy ease can be enjoyed. But Franklin recognized the struggle for existence, the workings of the inexorable laws of life, and that sooner or later neglect of the law of work brings realization that if we would eat we must work.

"Finally, let us consider Franklin's spirit and purpose in his life of work. He applied along scientific and economic lines the abilities of his mind and his hours of labor to broadening human knowledge and benefiting his fellowmen, not alone of his own generation, but with foresight and consideration for generations to come. And to this we must add his long, conspicuous and most able services in public capacities in trying colonial and revolutionary days—services so present in your minds that they speak for themselves, and evoke your gratitude.

"If we can absorb somewhat of spirit and purpose from the Franklin atmosphere which pervades this venerable Institute, the contemplation of his life will be to us an inspiration to work and serve."

The paper of the evening was presented by Dr. E. A. Eckhardt, Physicist, Bureau of Standards, Department of Commerce, Washington, D. C., on "Building Acoustics." The chief problems of acoustics which are encountered



in the construction and furnishing of public buildings and homes were outlined and it was pointed out that with the development of fireproof building construction the requirements of satisfactory acoustical conditions have been increasingly difficult to meet. The degree to which our present knowledge permits predetermination of acoustical properties of structures from their design was discussed. The direction and extent of present-day research along building acoustic lines was also reviewed. The subject was illustrated by lantern slides.

A unanimous vote of thanks was extended to Doctor Eckhardt for his paper.  
Adjourned.

R. B. OWENS,  
*Secretary.*

## COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday,  
January 3, 1923.)*

HALL OF THE INSTITUTE,  
PHILADELPHIA, January 3, 1923.

DR. JAMES BARNES *in the Chair.*

The following reports were presented for final action:

No. 2801	}	The Franklin Medal. The Franklin Medal to General G. Ferrié, Chief Signal Officer, French Army, Paris, France, and Dr. A. A. Michelson, Professor of Physics, University of Chicago, Chicago, Illinois.
and		
No. 2802		

The following reports were presented for first reading:

No. 2763: "Sip" Universal Measuring Machine.  
No. 2785: Maxon Pre-Mix Burner.  
No. 2798: Adjustable Hinge.

R. B. OWENS,  
*Secretary.*

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, January 10, 1923.)*

#### RESIDENT MEMBERS.

PROF. WILLIAM H. KAVANAUGH, University of Pennsylvania, Philadelphia, Pennsylvania.  
MR. LEWIS FERRY MOODY, William Cramp and Son's Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania.  
MR. J. HARRY MULL, William Cramp and Son's Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania.  
DR. HORACE C. PORTER, 1833 Chestnut Street, Philadelphia, Pennsylvania.  
MR. H. BIRCHARD TAYLOR, William Cramp and Son's Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania.



## NON-RESIDENT.

MR. CHARLES CHRISMAN, 405 West Miner Street, West Chester, Pennsylvania.

## CHANGES OF ADDRESS.

MR. JOHN H. BARR, Barr-Morse Corporation, 149 Church Street, New York City, New York.

MR. A. W. K. BILLINGS, in care of Canadian and General Finance Company, Ltd., 357 Bay Street, Toronto, Canada.

MR. W. F. GRAHAM, Curtis Bay Copper and Iron Works, Curtis Bay, Baltimore, Maryland.

MR. B. B. MILNER, Imperial Hotel, Tokyo, Japan.

## LIBRARY NOTES.

## PURCHASES.

AMERICAN SOCIETY FOR TESTING MATERIALS—Proceedings, 2 vols. 1922.

Jahresbericht über die Leistungen der chemischen Technologie für das Jahr, 1921, 2 vols. 1922.

KEINATH, GEORG—Die Technik der elektrischen Messgeräte, Ed. 2. 1922.

MALCOLM, H. W.—The Theory of the Submarine Telegraph and Telephone Cable. 1917.

MINERAL INDUSTRY—Its Statistics, Technology and Trade during 1921. 1922. Photograms of the Year 1922.

ROBINSON, CLARK SHOVE—The Recovery of Volatile Solvents. Ed. 1. 1922.

THORPE, SIR EDWARD—Dictionary of Applied Chemistry, vol. 4. 1922.

## GIFTS.

Abbe, Paul O., Catalogue H, Grinding, Mixing and Sifting Machinery. New York City, New York, 1922. (From Mr. Paul O. Abbe.)

Alabama Department of Mines, Annual Report for 1921. Birmingham, Alabama, 1922. (From the Department.)

American Chemical Paint Company, Bulletin No. 9-B. Philadelphia, Pennsylvania, 1922. (From the Company.)

American Society of Civil Engineers, Transactions, Vol. 85, 1922. New York City, New York, 1922. (From the Society.)

Australian Commonwealth Railways Department, Report, with Appendices on Commonwealth Railways. Melbourne, Australia, 1922. (From the Commonwealth Railways Commissioner.)

Baird Machine Company, Brief Bits 'Bout Baird Machinery. Bridgeport, Connecticut, 1920. (From the Company.)

Ballard, Sprague and Company, Ballard-Sprague Construction Service Boiler Settings and Chimneys. New York City, New York, 1922. (From the Company.)

Bartley, Jonathan, Crucible Company, Graphite Crucibles for Foundry Practice. Trenton, New Jersey, 1922. (From the Company.)

Bausch and Lomb Optical Company, Contour Measuring Projector. Rochester, New York, 1922. (From the Company.)



- Brown Instrument Company, Catalogue No. 90. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Bullard Machine Tool Company, Operator's Hand Book. Bridgeport, Connecticut, 1922. (From the Company.)
- Canada Department of Customs and Excise, Shipping Report for 1921-1922. Ottawa, Canada, 1922. (From the Department.)
- Canada Geological Survey, Bulletin 35. Memoir 130 and Summary Report, 1921, Parts B and E. Ottawa, Canada, 1922. (From the Survey.)
- Canada Water Power Branch, Water Resources Papers Nos. 1, 2, 3, 4, 7, 8, 13, 14, 16, 17, 18, 19, 21, 22, 23, 24, 25, 26 and 34; Annual Reports 1913-1915 and Folder of Maps. Ottawa, Canada. (From the Department.)
- Carnegie Endowment for International Peace, Year Book, 1922. Washington, District of Columbia. (From the Society.)
- Carnegie Steel Company, Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Pig Iron. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Case School of Applied Science, Catalogue 1922-1923. Cleveland, Ohio, 1922. (From the School.)
- Central Steel Company, Agathon Alloy Steels. Massillon, Ohio, 1922. (From the Company.)
- Century Wood Preserving Company, Treated Ties and Timbers for Industrial Plants. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Colorado Geological Survey, Bulletins 8 to 14, 17 to 19, 23 to 26, inclusive. Boulder, Colorado, 1914 to 1921. (From the State Geologist.)
- Colorado State Bureau of Mines, Bulletins 7 and 9, Annual Reports for 1920 and 1921, and Fourteenth Biennial Report for 1915-16. Denver, Colorado. (From the Bureau.)
- Combustion Engineering Corporation, Bulletin CB1, Coxe Stokers. New York, City, New York, 1922. (From the Corporation.)
- Cornell University, The Register, 1921-1922. Ithaca, New York, 1922. (From the University.)
- Detroit Stoker Company, Cutting the Cost of Producing Steam. Detroit, Michigan, 1922. (From the Company.)
- Disston, Henry, and Sons, Incorporated, Metal Cutting Saws. Philadelphia, Pennsylvania, 1922. (From the Corporation.)
- Dust Recovering and Conveying Company, Bulletins 6 and 8. Cleveland, Ohio, 1922. (From the Company.)
- Federated Engineers Development Corporation, Booklet describing the Organization of the Corporation. Jersey City, New Jersey, 1922. (From the Corporation.)
- Florida State Geological Survey, Thirteenth and Fourteenth Annual Reports. Tallahassee, Florida, 1921 and 1922. (From the State Geologist.)
- Foote, J. B., Foundry Company, Concrete Block Machinery and Concrete Mixers. Fredericktown, Ohio, 1922. (From the Company.)
- Fulton Company, Catalogue 100, Sulphon Heating Specialties. Knoxville, Tennessee, 1922. (From the Company.)
- General Motors Truck Company, Modern Freight Transportation. Pontiac, Michigan, 1922. (From the Company.)



- Griscom-Russell Company, Bulletin No. 904 Multiwhirl Color. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Homestead Valve Manufacturing Company, Homestead Valves. Homestead, Pennsylvania, 1922. (From the Company.)
- Hydro-High Vacuum Pump Company, Bulletin No. 100. Newport, Kentucky, 1922. (From the Company.)
- Idaho Mining Industry, 8th to 15th, 18th, 19th, 22nd and 23rd Annual Reports. Boise, Idaho, 1907 to 1922. (From the Mine Inspector.)
- Illinois Department of Mines, Annual Coal Report for 1921. Springfield, Illinois, 1921. (From the Department.)
- India Geological Survey, Records Vol. liv, Part 2. Calcutta, India, 1922. (From the Director.)
- Indiana Department of Geology and Natural Resources, Fortieth and Forty-first Annual Reports and Booklet on Kaolin of Indiana by W. N. Logan. Indianapolis, Indiana, 1915 and 1919. (From the State Geologist.)
- International Railway General Foremen's Association, Book of Proceedings. Winona, Minnesota, 1922. (From the Secretary.)
- Iowa State Mine Inspectors, Reports for 1915, 1917, 1920 and 1922. Des Moines, Iowa. (From the Department.)
- Johns Hopkins University, Catalogue and Announcement for 1922-1923. Baltimore, Maryland, 1922. (From the University.)
- Kansas Department of Mines, Coal Mine Inspection Reports for 1911 to 1916, 1920 and 1921. Topeka, Kansas. (From the Department.)
- Liberty Manufacturing Company, Catalogue Z-1. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Little, Arthur D., Incorporated, The Petroleum Outlook. Cambridge, Massachusetts, 1920. (From the Corporation.)
- Lodge and Shipley Machine Tool Company, Examples of Turning. Cincinnati, Ohio, 1922. (From the Company.)
- Logansport Machine Company, Air Operated Chucks and Labor-saving Devices. Logansport, Indiana, 1922. (From the Company.)
- Metal and Thermit Corporation, Booklet of Thermit Locomotive Repairs. New York City, New York, 1922. (From the Corporation.)
- Michigan Department of Labor, Thirty-seventh Annual Report and Mines Report. Lansing, Michigan, 1920. (From the Department.)
- Midwest Steel and Supply Company, Architects and Engineers Data Book, New York City, New York, 1922. (From the Company.)
- Missouri Bureau of Geology and Mines, Biennial Report of the State Geologist, for 1921. Rolla, Missouri, 1922. (From the State Geologist.)
- Murphy and Son, Limited, Bulletin No. 7 of Chemical and Physical Research Laboratory. London, England, 1922. (From the Company.)
- National Fire Protection Association, Year Book and Membership Directory, 1922. Boston, Massachusetts, 1922. (From the Association.)
- National Metal Molding Company, Catalogue No. 250. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- New Jersey Geological Survey, Bulletins 7, 8, 9, 10, 12, 16, 18, 19 and 21. Trenton, New Jersey, 1912 to 1921. (From the State Geologist.)



- New Zealand Census and Statistics Office. Results of a Census. April, 1921. Wellington, New Zealand, 1922. (From the Government Statistician.)
- Niagara Machine and Tool Works, Bulletin No. 58. Buffalo, New York, 1922. (From the Works.)
- Ödön, Wildner, Franklin Benjámín Öncéletrajza. Budapest, Hungary, no date. (From Rózsavölgyi and Company.)
- Protexol Corporation, Bulletins 40 and 41. New York City, New York, 1922. (From the Corporation.)
- Rathbone, A. B. and J., Pinion Rods and Cold Drawn Shapes. Palmer, Massachusetts, 1922. (From A. B. and J. Rathbone.)
- Royal Society of South Australia, Transactions and Proceedings, Vol. xlv. Adelaide, South Australia, 1922. (From the Society.)
- Sabin Machine Company, Sabin One-man Trucks. Cleveland, Ohio, 1922. (From the Company.)
- Scotland Institution of Engineers and Shipbuilders, Transactions of Sixty-fifth Session. Glasgow, Scotland, 1922. (From the Institution.)
- Sherman, H. B., Manufacturing Company, Sherman Fine Small Motors. Battle Creek, Michigan, 1922. (From the Company.)
- South Dakota Department of Mines, 23rd, 24th, 25th, 26th and 27th Annual Reports. Lead, South Dakota, 1912 to 1916. (From the Department.)
- South Dakota Geological Survey, Bulletins 5, 6, 7, 8, 9, 10 and Circulars 4, 6, 7, and 8. Vermillion, South Dakota, 1912 to 1922. (From the State Geologist.)

---

## PUBLICATIONS RECEIVED.

*Carotinoids and Related Pigments: The Chromolipoids*, by Leroy S. Palmer, Ph.D. 316 pages, illustrations, plates, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price, \$4.50.

*The New Air World. The Science of Meteorology Simplified*, by Willis Luther Moore, Sc.D., LL.D. 326 pages, illustrations, plates, 12mo. Boston, Little, Brown and Company, 1922. Price, \$3.00 net.

*Die Technik der elektrischen Messgeräte*, von Dr. Ing. Georg Keinath. Zweite erweiterte Auflage. 477 pages, illustrations, 8vo. München, R. Oldenbourg, 1922. Price, in paper, \$4.80.

*A Treatise on Weighing Machines: A Guide to the Principles Underlying the Construction of Weighing Instruments*, by George A. Owen. 202 pages, illustrations, plates, 8vo. London, Charles Griffin and Company, Ltd.; Philadelphia, J. B. Lippincott Company, 1922.

*Introduction to Plane Analytical Geometry and Differential Calculus*, by Clifford Newton Mills, B.S., M.A. 131 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1922. Price, \$1.50.

*The Microscopical Examination of Foods and Drugs*. A practical introduction to the methods adopted in the microscopical examination of foods and drugs, in the entire, crushed and powdered states, by Henry G. Greenish, F.I.C., F.L.S. Third edition, 386 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$4.50.



*Was ist die Mathematik?* Unterhaltungen während einer Seereise von Lothar Hefter. 160 pages, illustrations, 16mo. Freiburg i. B., Theodor Fisher, 1922. Price, in paper, 50 cents.

*United States Weather Bureau: Daily River Stages at River Gage Stations on the Principal Rivers of the United States.* Vol. xix for the year 1921, by H. C. Frankenfield, Meteorologist. 277 pages, quarto. Washington, Government Printing Office, 1922.

*United States Coast and Geodetic Survey: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory at Cheltenham, Maryland, 1919 and 1920,* by Daniel L. Hazard, Assistant Chief, Division of Terrestrial Magnetism. 97 pages, plates, quarto. Washington, Government Printing Office, 1922. Price, in paper, 30 cents. *Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory near Honolulu, Hawaii, 1919 and 1920,* by Daniel L. Hazard, Assistant Chief, Division of Terrestrial Magnetism. 97 pages, plates, quarto. Washington, Government Printing Office, 1922. Price, in paper, 20 cents. *Magnetic Declination in the United States for January 1, 1920,* by Daniel L. Hazard, Assistant Chief, Division of Terrestrial Magnetism. 30 pages, map, 8vo. Washington, Government Printing Office, 1922. Price, in paper, five cents.

*Questionnaire and Score Card Applicable in Choosing a Country Property,* by Dr. Wm. Paul Gerhard, C.E. 10 pages, 12mo. New York City, Author, 1922. Price, 30 cents.

*National Advisory Committee for Aeronautics: Technical Notes, No. 121, Further Information on the Laws of Fluid Resistance,* by C. Wieselberger. From *Physikalische Zeitschrift*, 1922, vol. 23. 8 pages, diagrams, quarto. No. 122, *The Determination of the Angles of Attack of Zero Lift and of Zero Moment, Based on Munk's Integrals,* by Max M. Munk. 9 pages, illustrations, quarto. No. 123, *An Optical Altitude Indicator for Night Landing,* by John A. C. Warner. 5 pages, illustrations, photograph, quarto. Washington, Committee, 1922.

*U. S. Bureau of Mines: Bulletin 209, Fusibility of Ash from Coals of the United States,* by W. A. Selvig and A. C. Fieldner. 119 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1922.

*Tenth Annual Report of the Secretary of Commerce 1922.* 231 pages, 8vo. Washington, Government Printing Office, 1922. Price 25 cents.

*The Universal Law of Organic Progress.* A colligated presentation by Daniel Nelson Clark, LL.B. 27 pages, illustrations, 8vo. Los Angeles, California, Ingersoll and Harrison, 1922. Price 15 cents.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

Vol. 195

MARCH, 1923

No. 3

## ANALYSIS OF AIRPLANE FACTORS.\*

BY

A. F. ZAHM, Ph.D.

Bureau of Construction and Repair, U.S.N.;  
Associate Editor.

### PREFACE.

It is sometimes useful to forecast the performance of an airplane from the known coefficients of its wing profile; also to compare by such means the performance of an airplane equipped successively with different wings. The airplane factors occasionally used in such forecast and comparison are here derived and graphically illustrated. The text is a slightly revised form of a report prepared for the Bureau of Aeronautics by the present writer, and dated June 1, 1922. The diagrams were made by Mr. R. M. Bear.

### I. WING FORCES AND COEFFICIENTS.

*Lift and Drag.*—The lift and drag of a wing model are the components of the air force respectively across and along the undisturbed direction of the air stream. The lift  $L$  and drag  $D$  of an aerofoil of area  $S$ , in straight and steady translation at speed  $V$ , through air of density  $\rho$ , may be written

$$L = C_L \frac{\rho}{2} S V^2 \dots \dots \dots (1)$$

$$D = C_D \frac{\rho}{2} S V^2 \dots \dots \dots (2)$$

\* Communicated by the Author.

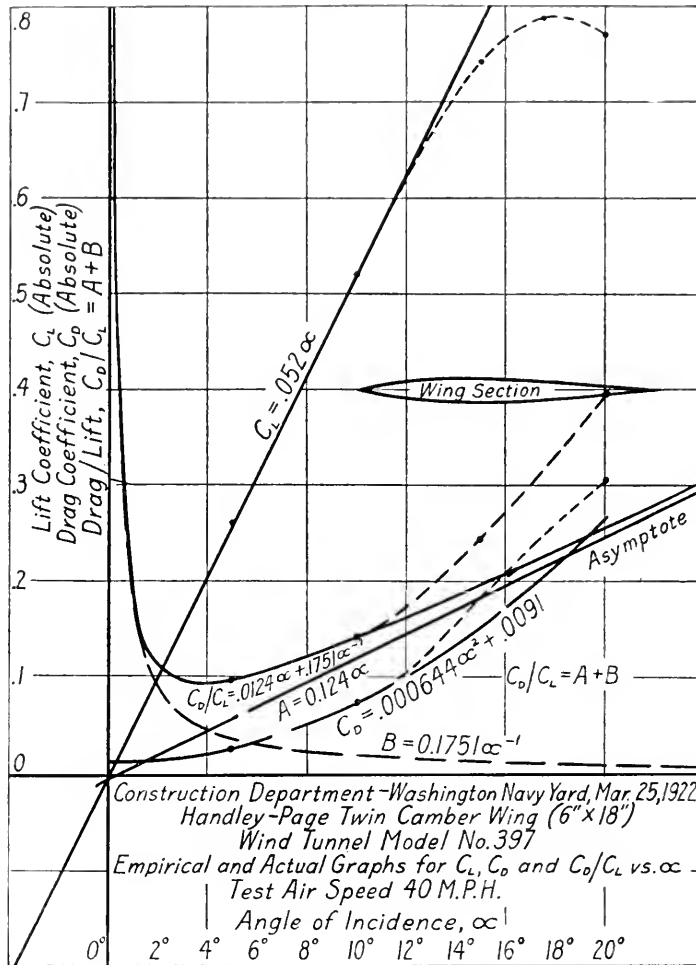
(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.



where  $C_L$  and  $C_D$  are shape coefficients which, for simplicity, are assumed to be fairly constant while the shape and presentation of the model to the wind remain fixed. In (1), (2), and throughout this text, one ignores the value of Reynold's number  $Vl/\nu$ ,

FIG. 1.



where  $\nu$  is the kinematic viscosity of the air, and  $l$  is some length such as the span or chord of the wing.

*Lift and Drag Coefficients.*—For a great variety of aerofoils the lift is a linear, the drag a quadratic function of the angle of attack  $\alpha$ , when this ranges through the usual flying incidences. Hence if  $\alpha$  is referred to the wing chord

$$C_L = a'\alpha + b' \dots \dots \dots (3)$$

$$C_D = c'\alpha^2 + d'\alpha + e' \dots \dots \dots (4)$$

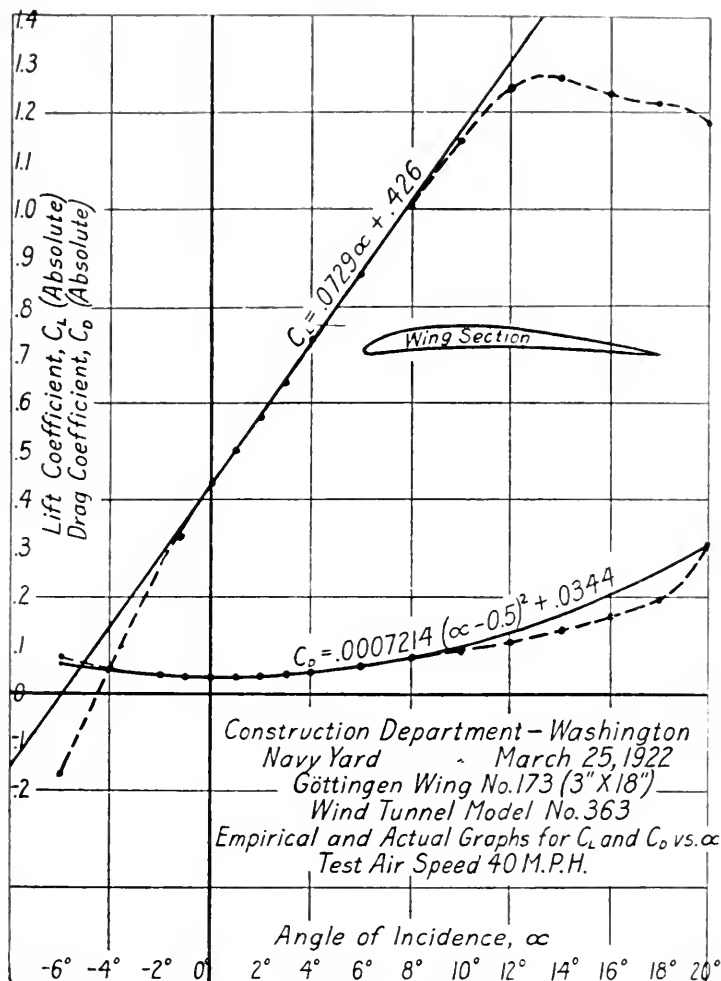
$$= a C_L^2 + b C_L + c \dots \dots \dots (5)$$



in which all the small-letter coefficients are constants easily obtainable from the experimental lift and drag diagrams. From (3), (4), (5), it is easily found that

$$\begin{aligned} a &= c'/a'^2 \\ b &= (a'd' - 2b'c')/a'^2 \quad \dots \dots \dots (6) \\ c &= (b'c' - a'b'd' + a'^2e')/a'^3 \end{aligned}$$

FIG. 2.



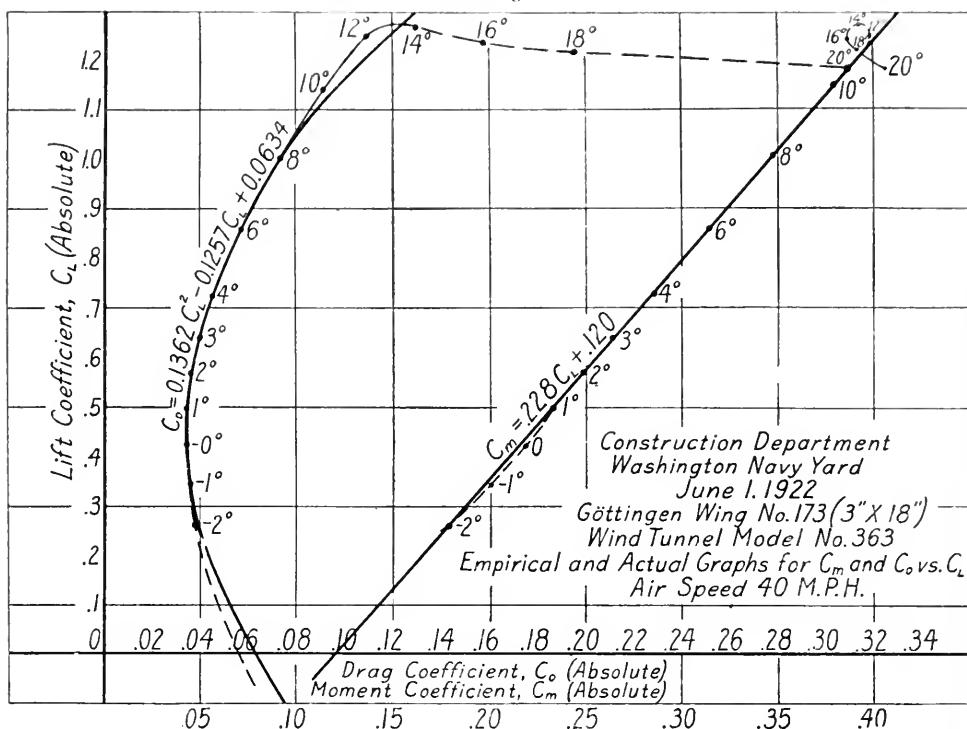
For a twin-camber wing, for which  $b' = 0$ , (3) is the straight line  $C_L = a'\alpha$  through the origin; (4) is the parabola  $C_D = c'\alpha^2 + e'$ , with its vertex at  $(0, e')$ ; (5) becomes  $C_D = a C_L^2 + c$ , where  $c = e'$ . Thus all the second terms of the second members of (3), (4), (5), are zero. For many shapes also of wings not twin-cambered  $d'$  and  $b C_L$  are zero while  $b'$  is not. If  $\alpha$  is referred to the null line,  $b' = 0$  always.  $C_L / C_D$  versus  $\alpha$  is a



cubic;  $C_D / C_L$  versus  $\alpha$  a hyperbola (Fig. 1). Also  $D/L$  versus  $\alpha$  is a hyperbola; hence  $D$  versus  $\alpha$  is, too, when  $L$  is a constant load.

The accuracy of (3) and (4) in two favorable cases is illustrated in Figs. 1 and 2; and the accuracy of (5) is disclosed in Fig. 3. The equations to these curves are purely empirical, that is, they are made to accord with faired wind-tunnel data irrespective of

FIG. 3.



any physical theory. In general, the wind-tunnel lift and drag for a considerable range of incidence can not be simply and perfectly expressed by either rational or empirical formulæ. The present illustrations show that the actual lift and drag coefficients sometimes can be algebraically expressed with sufficient precision to be practically useful.

**Pitching Moment Coefficient.**—In general  $L$  and  $D$  exert a pitching moment  $M$  about any transverse line, say the leading edge of the wing. The coefficient of pitching moment is usually written

$$C_m = M / \frac{\rho}{2} c S V^2 \dots\dots\dots (7)$$

where  $c$  is the mean chord length of the wing. For many aerofoils

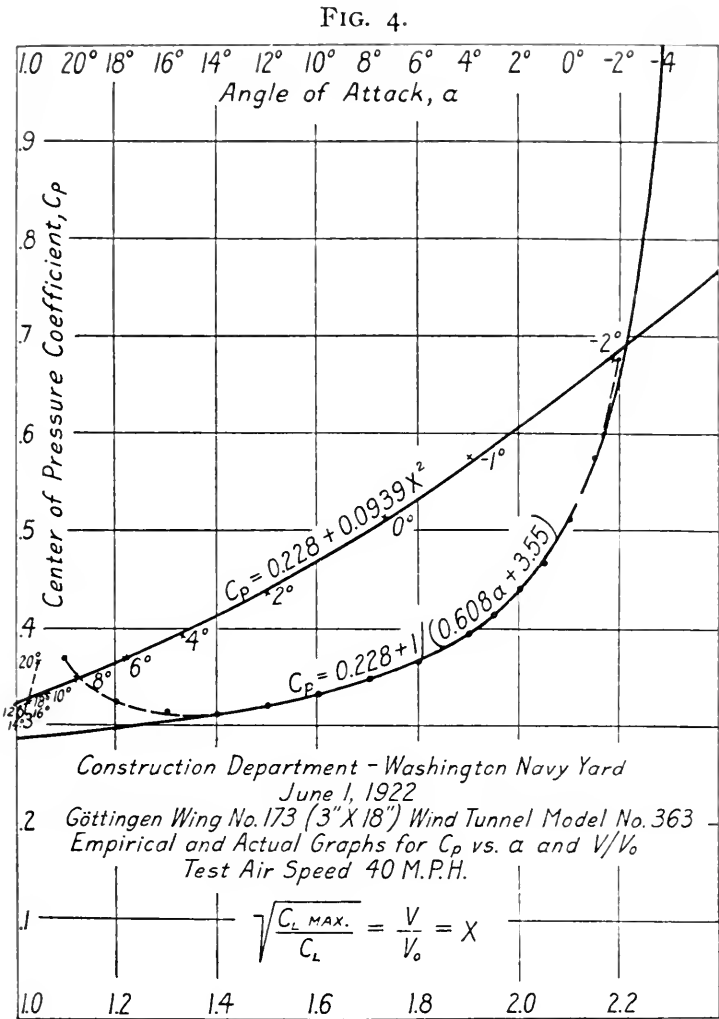


$C_m$ , for  $\alpha$  small, is a linear function of  $C_L$ , as shown in Fig. 3, in which it has the form

$$C_m = fC_L + g \dots\dots\dots (8)$$

Hence when  $f$  and  $g$  are constants,  $C_m$  plots against  $C_D$  as a parabola, as illustrated in Fig. 3.

*Centre of Pressure Coefficient.*—If  $l$  is the distance of the centre of pressure from the leading edge, one may write approxi-



mately  $M = Ll$ , for small angles of attack and large efficiency  $L/D$ . Then (7) becomes

$$l'c = C_m/C_L = C_r \dots\dots\dots (9)$$

where  $C_r$  is the centre of pressure coefficient. And since  $C_m = fC_L + g$ , (9) becomes, for these small angles,

$$C_r = f + g/C_L \dots\dots\dots (10)$$

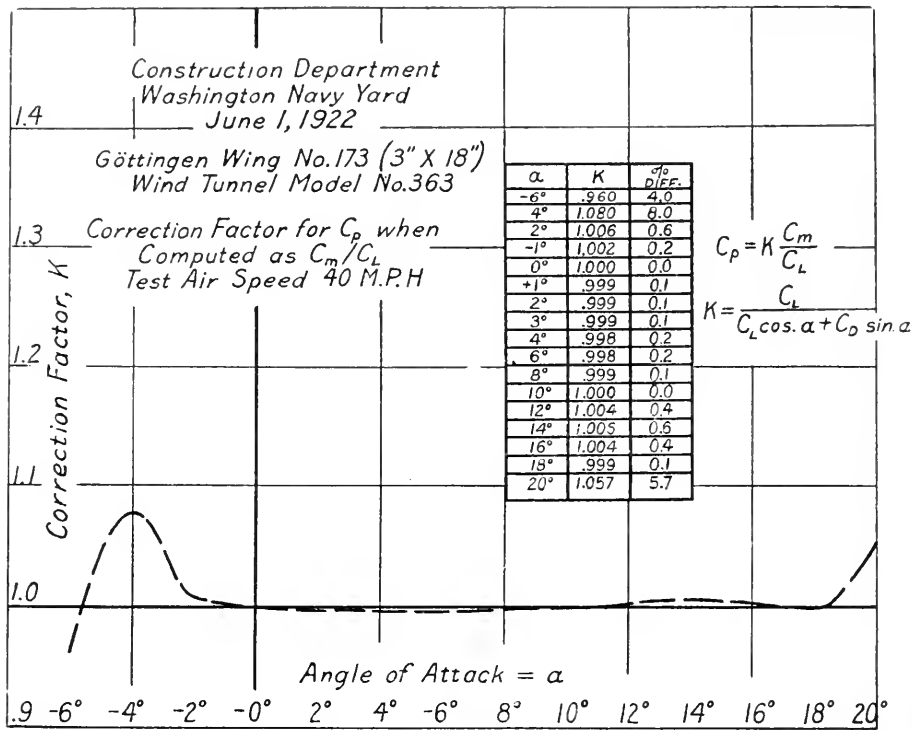


or the distance  $l$  of the centre of pressure, for such conditions, is a quadratic function of the speed  $\sqrt{C_L \text{ max}/C_L}$  as given by (11) below. Fig. 4 shows the agreement of (10) with the experimental data for a typical wing. The more familiar graph of  $C_p$  versus  $\alpha$ , shown in Fig. 4, is the hyperbola got from (3) and (10),

$$C_p = f + g/(a'\alpha + b') \dots\dots\dots (10_1)$$

When the range of  $\alpha$  is large, one should write, for exact-

FIG. 5.



ness,  $M = l(L \cos \alpha + D \sin \alpha)$ ; that is (9) and (10) must be multiplied by the correction factor  $C_L / (C_L \cos \alpha + C_D \sin \alpha)$ . The value of this factor plotted against  $\alpha$  is given in Fig. 5 for a typical aerofoil. It differs from unity, for  $\alpha$  between  $0^\circ$  and  $10^\circ$ , by a small fraction of 1 per cent.

In engineering practice, for the more usual flying angles, one finds  $l$  numerically as  $l = M/L$  or  $cC_m/C_L$ ; and graphically by drawing a straight line through the origin on a diagram of  $C_m$  versus  $C_L$  to cut this curve at  $(C_m, C_L)$  and to cut the line  $C_L = c$  at a point which by (10) must necessarily be  $(l, c)$ , and hence gives  $l$  directly. This graphic method is applicable also to

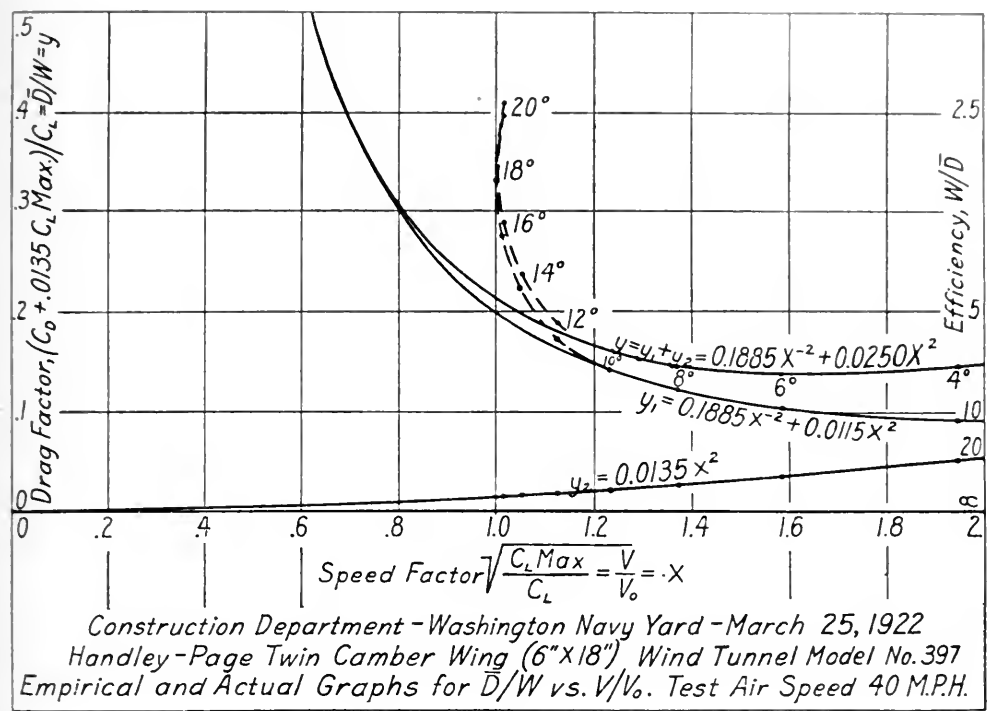


the  $M$  versus  $L$  diagram where the straight line  $L = 1$  is cut at the point  $(1, 1)$ .

II. AIRPLANE FACTORS.

*The Speed Factor.*—If the weight,  $W = \frac{1}{2} C_L \rho S V^2 = L$ , of

FIG. 6.



an airplane in straight horizontal translation is sensibly constant, the speed  $V$  can be written

$$V = V_0 \sqrt{\rho_0/\rho} \sqrt{C_{L\text{ max}}/C_L}, \dots\dots\dots (11')$$

or

$$V = V_0 \sqrt{C_{L\text{ max}}/C_L}, \text{ for } \rho \text{ constant } \dots\dots\dots (11)$$

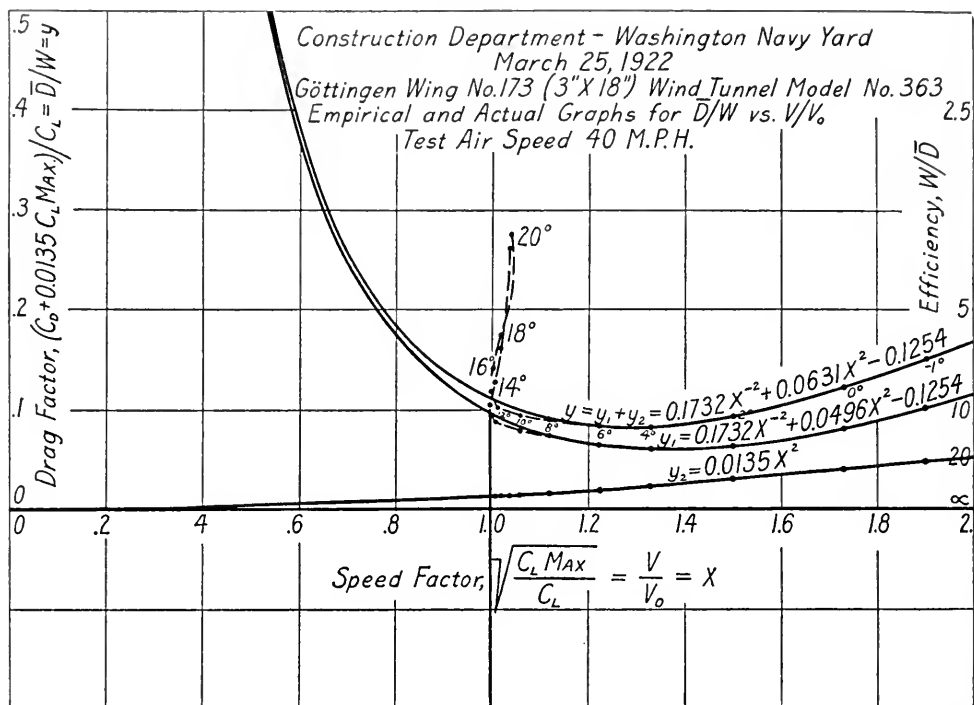
in which  $C_L$  is the wing-lift coefficient, and the multiplier of  $V_0$  in (11) is called the "speed factor." This latter is the actual speed in terms of the slowest speed,  $V_0 = \sqrt{2W/C_{L\text{ max}} \rho_0 S}$ , as unit.

*Density Factor.*—If the air density varies, one obviously must use the form (11') wherever  $V$  enters as a factor. Unless otherwise stated,  $\rho$  in the following text will be assumed constant, that is, the "density factor"  $\sqrt{\rho_0/\rho} = 1$ .



*The Drag Factor.*—The drag  $\bar{D} = \frac{1}{2}\rho S V^2 (C_D + C'_D)$ , of said airplane, comprises two terms: The first being the main planes drag, whose coefficient is  $C_D$ ; the second being an addition to  $C_D$  to represent the parasite resistance. In practice it appears that one may write  $C'_D = n C_L \max$ , where  $n$  is a numeral averaging about .0135 for different machines, and not greatly different for

FIG. 7.



various types. Using  $n$  and noting that  $\frac{1}{2}\rho S V^2 = W/C_L$ , the drag becomes

$$\bar{D} = W(C_D + n C_L \max)/C_L \dots \dots \dots (12)$$

whose multiplier of  $W$  is called the “drag factor.” It is the actual drag in terms of  $W$  as unit. One should distinguish  $\bar{D}$  of (12) from  $D$  of (2).

*Power Factor.*—Multiplying the drag by the speed  $V$  gives the towline power

$$P = W V_0 \sqrt{C_L \max / C_L} (C_D + n C_L \max)/C_L \dots \dots \dots (13)$$

whose multiplier of  $W V_0$  is called the “power factor.” It is the actual power in terms of  $W V_0$  as unit. If the density varies, the power factor obviously must be multiplied by the density factor  $\sqrt{\rho_0/\rho}$ , as shown in (11’).



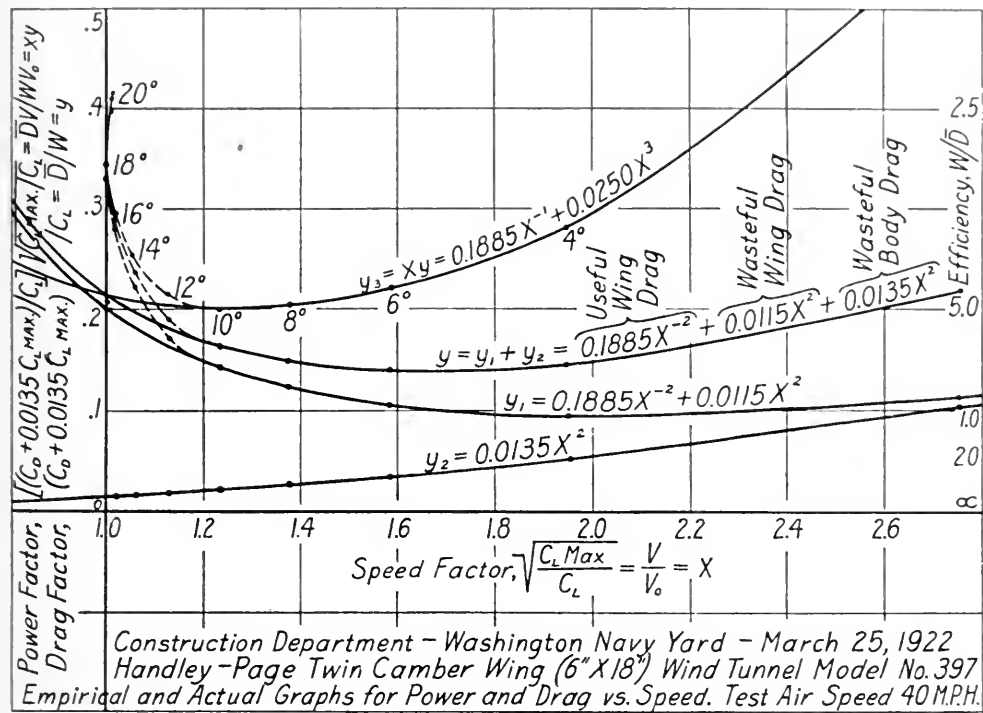
It sometimes is assumed that at high speed  $C_D = n C_L \max$ ; hence  $C_D^2/C_L^3 \propto P^2$ . In any case

$$(C_D + n C_L \max)^2 / C_L^3 \propto P^2 \dots\dots\dots (131)$$

III. PERFORMANCE OF CONSTANT-WING AIRPLANE.

*Drag-speed Curve.*—Plotting the drag factor against the speed factor, as in Figs. 6 and 7, gives the drag-speed curve corre-

FIG. 8.



lating  $\overline{D}/W, = \overline{D}/L$ , with  $V/V_0$ ; thus exhibiting the drag, or thrust, and the efficiency  $L/D$  as functions of the speed. The equation of this curve is, by (12),

$$\overline{D}/W = (C_D/C_L \max + n) C_L \max / C_L \dots\dots\dots (14')$$

or

$$y = (m C_D + n) x^2, \dots\dots\dots (14)$$

where  $y = \overline{D}/W$  is the drag factor,  $x$  the speed factor, and  $m = 1/C_L \max$ .

Since  $n$  is known, and since at the lowest speed  $V/V_0 = 1 = x$ , the whole drag  $\overline{D}$  and efficiency  $W/\overline{D}$  are determinate for this speed; the latter absolutely, the former relatively to the weight. At sufficiently high speed, which means small incidence,  $C_D$



is nearly constant and a minimum, making the curve (14) substantially parabolic, and of the form  $y = (C_D \text{ min}/C_L \text{ max} + n)x^2$ .

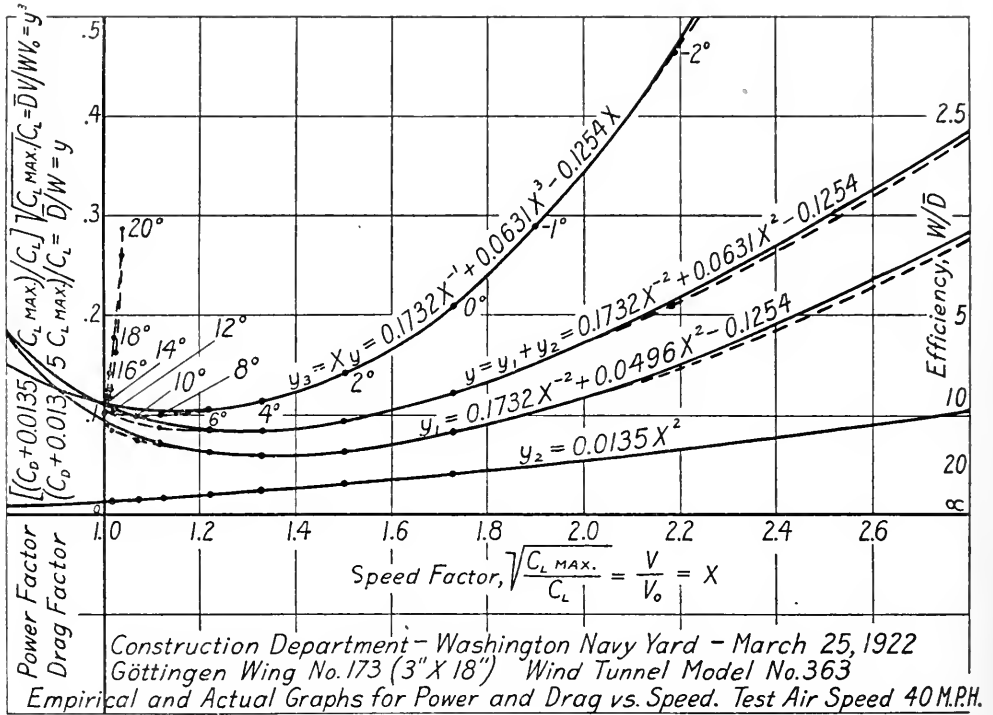
In general the drag-speed curve (13) is compounded of the two parts

$$y_1 = m C_D x^2 = C_D/C_L \dots\dots\dots (15)$$

$$y_2 = n x^2 = n C_L \text{ max}/C_L \dots\dots\dots (16)$$

due to the drags respectively of the wing group and of the body group. The latter is a parabola in  $x$  with its vertex at  $x = 0 = V$ .

FIG. 9.



The former readily can be written as a simple function of  $x$  when  $C_D$  is a parabolic function of  $C_L$ , as given by (5), on noting that  $C_L = C_L \text{ max}/x^2$ .

Thus substituting from (5) in (15) gives

$$y_1 = (a C_L^2 + b C_L + c)/C_L \dots\dots\dots (17')$$

$$= a_1 x^{-2} + b + c_1 x^2 \dots\dots\dots (17)$$

where  $a_1$  and  $c_1$  are the new constant coefficients due to the indicated algebraic operation, viz.,

$$\left. \begin{aligned} a_1 &= a C_L \text{ max} \\ c_1 &= c/C_L \text{ max} \end{aligned} \right\} \dots\dots\dots (18)$$

One sees by (17) that  $y_1$  is the sum of two functions, one hyper-



bolic in type, the other parabolic, as featured by the  $y_1$  graph in Figs. 6 and 7. For a twin-camber wing  $b = 0$ , as previously explained.

Incidentally one notes that  $y_1$  *versus*  $\alpha$  is a hyperbola, since  $C_D/C_L$  is such, as seen in Fig. 1, and  $y_1 = C_D/C_L$ , by (15).

Adding (16) and (17) gives the drag as an explicit function of the speed, or

$$y = a_1 x^{-2} + b + (n + c_1) x^2 \dots \dots \dots (19)$$

$$= a_1 x^{-2} + (n + c_1) x^2 \text{ for twin-camber wings } \dots \dots (19_1)$$

This curve tends to the hyperbolic type as  $x$  approaches zero; has a minimum for ordinary flying speeds, *i.e.*, for  $x = V/V_0 > 1$ ; and becomes parabolic for sufficiently high speeds. It is delineated in Figs. 6 and 7, as the sum of the component curves  $y_1, y_2$ . The minimum occurs at the point where  $x^4 = a_1/(n + c_1) = x_m^4$ , and has the value

$$y_m = a_1 x_m^{-2} + b + (n + c_1) x_m^2 = 2 \sqrt{a_1 (n + c_1)} + b \dots \dots (20)$$

This minimum drag, of course, occurs at the speed for which  $L/\bar{D}$  is a maximum, as illustrated in Figs. 6 and 7.

It is noteworthy that (19<sub>1</sub>) contains three drag terms, with  $W$  as the unit of force. The first,  $a_1 x^{-2} = a C_L$ , is the pressural wing drag, and varies inversely as the square of the speed. Hence the power to overcome it varies inversely as the speed, as De Bruignac proved for a frictionless plane in 1875, and as Langley thought he proved more than a decade later. The third term,  $c_1 x^2 = x^3 c/C_L \max = C_D \min/C_L$ , is, at least for thin planes, the frictional wing drag; for, as seen by (18) and (5), it is the actual wing drag at zero angle of attack, for which the pressural drag is nil. To be more exact the exponent of  $x$  should be about 1.85. The separation of the drag of a thin material plane into pressural and frictional parts was first made by the writer nearly two decades ago.<sup>1</sup> The second term  $n x^2$  is of course the body drag, as previously stated.

*Power-speed Curve.*—Multiplying (17) by  $V/V_0 = x$  gives the power-speed equation,

$$y' = a_1 x^{-1} + b x + (n + c_1) x^3 \dots \dots \dots (21)$$

$$= a_1 x^{-1} + (n + c_1) x^3 \text{ for twin-camber wings } \dots \dots (21_1)$$

<sup>1</sup> *Bull. Phil. Soc. Wash.*, vol. xiv, p. 272.



in which  $y' = P/IVV_o$  is the power factor, and the other symbols retain their former meaning. In Figs. 8 and 9, the power-speed curve is plotted with the drag-speed curve for an airplane having the two previously assumed wings. Obviously (21) tends to become a hyperbola for  $x$  nearing zero; a cubical parabola for  $x$  sufficiently large. At the slowest practicable speed, for which  $x = 1 = V/V_o$ , the drag and power factors (19) and (21) become identical.

By equating to zero the derivative of (21), or by multiplying (20) by  $x$ , one readily finds the minimum power factor. For a twin-camber wing, or any other giving  $b_1 = 0$ , it is

$$y'_m = a_1 x_m^{-1} + (n + c_1) x_m^3 = 1.75^4 \sqrt{a_1^3 (n + c_1)} \dots \dots \dots (22)$$

at the point where  $x^4 = a_1/3(n + c_1) = x_m^4$ . For wings not giving  $b = 0$  the value of  $x_m$ , obtained in the same way, is more cumbersome.

In (21<sub>1</sub>) the first term is the power consumed by the "useful" wing drag, and varies inversely as the speed  $x$ ; the second term  $nx^3$  is the power for the body drag; the third term is the power for the wasteful wing drag, and for thin planes varies more nearly as  $x^{2.85}$ . The term  $bx$  in (21) can best be understood by reference to the definition of  $b$  in (6).

*Agreement of the Algebraic and Empiric Graphs.*—For the assumed twin-camber wing the actual lift and drag, or their coefficients, are perfectly represented for flying angles under  $10^\circ$  by algebraic equations, as shown in Fig. 1. Hence the mathematical graphs of drag and power *versus* speed, for the same range of incidence, perfectly coincide with the corresponding empiric graphs, as seen in Figs. 6 and 8. For the higher angles of attack, approaching that of maximum lift, there is a sharp departure of the lift and drag data from the linear and quadratic laws, and hence a proportionate separation of the derived curves for speed and power.

For the other aerofoil the lift and drag data obey these laws perfectly at flying incidences below  $8^\circ$ , but not for higher angles, as seen in Fig. 2; hence the drag and power curves show a like discrepancy in Figs. 7 and 9. For wings like the present ones, therefore, the strictly mathematical expressions for required thrust and power, at all but the highest flying incidences, are as trustworthy as those found by plotting the tabulated values.



*Alternate Forms for the Graphs.*—The comparison of the work quantities so far plotted, *viz.*, drag, power and speed, sometimes can be made by suitably plotting functions of them. For example, to find what value of the speed,  $V/V_0 = \sqrt{C_{L\max}/C_L}$ , will require the least power, one may either note the minimum point on the graph of (13), or the minimum for (13<sub>1</sub>), or the maximum for  $C_L/(C_D + n C_{L\max})$  versus  $\sqrt{C_L/C_{L\max}}$ . Again, to find what speed will require least thrust, one may either note the minimum point on the graph of (12), or the square of (12), or the maximum on the inverse curve which results from reciprocating the ordinates of (12), or the maximum on the doubly inverse curve, etc. The methods of plotting, being so manifold, can best be chosen to suit the work in hand. The present graphs directly correlate familiar quantities. But to compare the aerodynamic merits of different aerofoils it sometimes may be well to plot simpler expressions, or to compare suitable criteria which can be derived from the foregoing equations.

#### SUMMARY.

The main doctrines of this report may be summarized as follows:

##### *Wing Forces and Moments.*

1. The lift, drag and pitching moment of a wing of fixed size, shape and presentation, moving uniformly, are proportional to the density and square of the speed, no account of Reynold's number being taken.
2. The lift and drag increase as the square, the moment as the cube, of the linear dimensions of the wing.
3. For the more usual angles of attack  $\alpha$ , the lift is a linear, the drag a quadratic function of  $\alpha$ ; hence the drag is a quadratic function of the lift.
4. The lift/drag is a cubic in  $\alpha$ ; the drag/lift is a hyperbola in  $\alpha$ ; hence the *drag versus*  $\alpha$  is a hyperbola where the lift is constant.
5. The pitching moment is a linear function of the lift; and hence plots against the drag as a parabola.
6. The distance of the centre of wing pressure aft of the leading edge is approximately  $l = M/L = cC_m/C_L$ ,  $c$  being the chord length;  $l$  plots against  $L$  as a hyperbola, against  $\alpha$  as a hyperbola, and, with constant loading, plots against speed as a parabola.



*Airplane Drag and Power.*

7. The drag of an airplane consists of the "useful" or pres-sural wing drag, the wasteful wing drag which is mainly frictional, and the body drag. The two latter vary closely as the square of the speed; the first varies inversely as the square of the speed, if the wing load is constant. The drag-*versus*-speed graph is therefore a kind of quartic, composed of a parabola and an inverse parabola or kind of hyperbola.

8. The towline power of an airplane therefore consists of the useful part which varies inversely as the speed, and the wasteful part which increases roughly as the cube of the speed. The power-speed graph is compounded of a hyperbola and a cubical parabola.

9. Expressions are given for the minimum drag and towline power in terms of the speed of the airplane.

**The Motion of a Sphere in a Rotating Liquid.** G. I. TAYLOR. (*Proc. Royal Soc.*, A 715.)—There are great mathematical difficulties in the way of theoretical investigations of the motion of a sphere in a rotating liquid, but these can be overcome in the case when the sphere moves with uniform velocity along the axis of rotation of the liquid. The equations show that then there is around the sphere a sheath of liquid which does not rotate as the rest of the liquid does. This deduction from theory was confirmed by experiment. It was arranged that a cylinder of liquid was rotated about its axis. A ping-pong ball was supported by a thread passing up along the axis of the vertical cylinder. The ball took up the rotation of the liquid. Then a uniform vertical velocity was given to the ball by means of the thread. "It was found that the ball stopped rotating directly it started moving along the axis. As soon as the reel was released, so that the ball stopped moving along the axis, it quickly picked up the rotation of the rest of the system once more. To ensure success, it was found necessary also to make the ball move at a rate greater than about one diameter per revolution of the system. If the ball travelled more slowly than this it was found that it did not stop rotating and investigation of the stream-lines, with colored water, showed that a column of liquid of the same diameter as the sphere was apparently pushed along in front of the sphere.

"In the course of these experiments, it was noticed that if the sphere was stopped suddenly when half-way up the cylinder, and if there was some coloring matter present to show up the motion, a mass of liquid appeared to detach itself from the sphere, and to continue moving along the axis of rotation with the same velocity as that with which the sphere had been moving."

G. F. S.



# A STUDY OF THE PLASTICITY OF PAINT.\*

BY

EUGENE C. BINGHAM, Ph.D., HERBERT D. BRUCE, M.S., AND  
MARTIN O. WOLBACH, Jr., M.S.

Lafayette College, Easton, Pennsylvania.

## INTRODUCTION.

It has been shown by Bingham and Hyden<sup>1</sup> that a colloidal solution of the polar type, such as we have when nitrocellulose is dispersed in acetone, does not possess a *definite fluidity*, as fluidities are customarily measured, for the reason that all solutions even at low concentration show the properties of plastic materials. The question now arises, Do non-polar colloids, such as clay suspended in water, require a plastic correction? The experiments of Bingham and Durham<sup>2</sup> and other investigators were not made under conditions which enable us to answer this question, but in view of the considerations set forth in the paper by Bingham and Hyden we must certainly regard their measurements of fluidity as *apparent fluidities* only, subject to a possible plastic correction.

Although learned very slowly, the method of attacking this problem now seems entirely obvious and simple. It is merely necessary to measure the flow of some suspensions at various shearing stresses and then observe whether the flow is directly proportional to the shearing stress or not.<sup>3</sup>

## MATERIALS AND METHOD OF MEASUREMENT.

Ready-mixed paints are quite complex, hence we have made up suspensions for our study from Gold Seal Beckton White Lithopone and Pure Acid Refined Linseed Oil, samples of which were furnished us by the E. I. du Pont de Nemours and Company.

In a quantitative investigation it is not practicable to grind the paint between burrstones in the ordinary manner. Rubbing out by hand seemed equally out of the question, due to the difficulty of grinding an adequate sample to a uniform consistency.

---

\* Communicated by Dr. Bingham.

<sup>1</sup> This JOURNAL, vol. 194, p. 731.

<sup>2</sup> "Fluidity and Plasticity," pp. 201-208.

<sup>3</sup> Cf. Bingham and Bruce, *Proc. Am. Soc. for Testing Materials*,—(1922).



We therefore used an Abbé porcelain ball-mill 22 x 24 cm. and the paint was ground for sixteen hours at a speed of 88.5 r.p.m.

Another investigation has been planned to determine the length of time which is necessary to give a constant plasticity and whether excessive grinding will affect the plasticity. There seems to be no question but that the micellian structure is being developed for a very long time after the grinding is started. In our present study of the subject, this particular question does not enter in, since we have made up a single paste and then obtained the others which we desired by thinning down with the pure oil.

The materials were used in their air-dry condition, but we have good reason to believe that small amounts of water may greatly affect the plasticity, hence in a later investigation it will be necessary to determine the effect of water and certain other substances such as soaps and free acids. The constants of the oil are as follows:

Iodine number .....	182.5
Saponification number .....	195.0
Acid number .....	4.13
Density 20/4° .....	0.9267
Refractive index at 20° .....	1.4810

It seems hardly practicable to make the conditions the same in grinding two different pigments, particularly when vehicles of very different fluidities are used. Even if the same mill is used with the same amount of balls of a given size and the speed is kept constant, the plasticity of the resulting paint is supposed to vary widely, hence the approach of the balls to each other will be very different and also the resulting grinding effect.

To the original sample successive additions of oil were made and mixed thoroughly by stirring for twenty minutes. The paint was then screened through a 300-mesh seive, placed in the plastometer and measured after standing for an hour in a constant temperature bath. Particularly with the thinner mixtures it was necessary to stir the paint again immediately before the measurement was made. All of the measurements were made at 25° C., except those given in Table IV, which were made at 20°. They are given in the order in which they were made.

Capillary No. 13 was the only one used in this investigation.



It had the following dimensions which had been measured by Mr. William R. Bender :

Length .....	5.018 cm.
Radius by mercury .....	0.01458 cm.
Average minor radius .....	0.01385 cm.
Average major radius .....	0.01534 cm.
Average radius calculated .....	0.01456 cm.

In order to obtain the yield value  $f$ , the best linear equation for the measurements on a given paint at different shearing stresses  $F$  was found by the method of averages,<sup>4</sup> and the intercept calculated. The efflux per second in grams is represented by  $M/t$  and the density by  $\rho$ . The mobility  $\mu$  was then found as in the preceding paper by Bingham and Hyden.

TABLE I.

*Plasticity of Paint Consisting of 65 per cent. Lithopone by Weight and 35 per cent. Linseed Oil.*

$f=128.1$   
 $\mu=0.4412$   
 $\rho=1.885$   
 $t=25^{\circ}$

$M/t=0.000001983$   
 $F=0.0002839$

Shearing Stress Dynes per cm. <sup>2</sup>	Efflux g. per second—Observed.	Efflux g. per second—Calculated.	Percentage Deviation.
498.2	0.000746	0.000734	— 1.6
498.1	0.000746	0.000734	— 1.7
753.8	0.001247	0.001242	— 0.5
753.7	0.001246	0.001240	— 0.5
930.7	0.001594	0.001591	— 0.2
930.5	0.001580	0.001591	+ 0.7
1111.3	0.001943	0.001949	+ 0.3
1110.8	0.001927	0.001949	+ 1.1
1355.0	0.002438	0.002433	— 0.2
1354.8	0.002420	0.002433	+ 0.5
1525.8	0.002760	0.002772	+ 0.6
1525.4	0.002743	0.002770	+ 1.0
1698.3	0.003127	0.003113	— 0.4
1698.0	0.003136	0.003113	— 0.7
1882.5	0.003457	0.003477	+ 0.6
1885.8	0.003515	0.003485	— 0.9
			0.7 Ave.

<sup>4</sup>Lipka, "Graphical and Mechanical Computation," p. 127.



TABLE II.

*Plasticity of Paint Consisting of 65 per cent. Lithopone by Weight and 35 per cent. Linseed Oil at 20° C.*

$f=145.5$   
 $\mu=0.3629$   
 $\rho=1.891$   
 $t=20^{\circ}\text{C.}$

$M/t=0.000001662 \text{ F} - 0.0002418$

Shearing Stress.	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
1888.7	0.002886	0.002898	+ 0.4
1892.3	0.002901	0.002903	— 0.1
1701.3	0.002594	0.002586	— 0.3
1697.1	0.002574	0.002579	+ 0.2
1494.5	0.002252	0.002243	— 0.4
1490.5	0.002245	0.002237	— 0.4
1307.3	0.001926	0.001931	+ 0.3
1310.9	0.001942	0.001938	— 0.2
1133.4	0.001642	0.001642	0.0
1132.9	0.001628	0.001642	+ 0.9
922.5	0.001295	0.001293	— 0.2
922.4	0.001288	0.001291	+ 0.2
662.2	0.000868	0.000859	— 1.1
662.0	0.000859	0.000859	0.0
			0.3 Ave.

TABLE III.

*Plasticity of Paint Consisting of 62.5 per cent. Lithopone by Weight and 37.5 per cent. Linseed Oil.*

$f=114.5$   
 $\mu=0.5257$   
 $\rho=1.815$   
 $t=25^{\circ}$

$M/t=0.000002311 \text{ F} - 0.0002648$

Shearing Stress.	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
639.4	0.001211	0.001213	+ 0.2
640.9	0.001221	0.001217	— 0.3
804.5	0.001599	0.001595	— 0.2
804.2	0.001589	0.001594	+ 0.3
977.1	0.001992	0.001994	+ 0.1
976.7	0.001987	0.001993	+ 0.3
1195.9	0.002504	0.002500	— 0.2
1191.7	0.002492	0.002491	0.0
1381.7	0.002966	0.002930	— 1.2
1381.2	0.002951	0.002927	— 0.8
1547.9	0.003307	0.003313	+ 0.2
1543.6	0.003268	0.003304	+ 1.1
1864.5	0.004042	0.004046	+ 0.1
1858.0	0.003997	0.004030	+ 0.8
			0.4 Ave.



TABLE IV.

*Plasticity of a Paint Consisting of 60 per cent. Lithopone by Weight and 40 per cent. Linseed Oil.*

$f=107.6$   
 $\mu=0.617$   
 $\rho=1.747$   
 $t=25^{\circ}$

$M/t=0.000002612 F - 0.0002811$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
1866.0	0.004592	0.004593	0.0
1865.4	0.004586	0.004590	+ 0.1
1689.4	0.004136	0.004130	— 0.2
1688.8	0.004148	0.004130	— 0.4
1516.7	0.003619	0.003681	+ 1.7
1516.1	0.003696	0.003678	— 0.5
1326.9	0.003194	0.003185	— 0.3
1326.6	0.003190	0.003185	— 0.2
1127.9	0.002673	0.002665	— 0.3
1121.7	0.002625	0.002649	+ 0.9
896.1	0.002065	0.002059	— 0.3
895.9	0.002030	0.002059	+ 1.3
656.8	0.001440	0.001434	— 0.4
			0.6 Ave.

TABLE V.

*Plasticity of a Paint Consisting of 55 per cent. Lithopone by Weight and 45 per cent. of Linseed Oil.*

$f=61.5$   
 $\mu=0.788$   
 $\rho=1.630$   
 $t=25^{\circ}$

$M/t=0.000003110 F - 0.0001912$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
648.4	0.001814	0.001826	+ 0.6
648.1	0.001829	0.001825	— 0.2
924.4	0.002680	0.002684	+ 0.1
922.2	0.002689	0.002677	— 0.4
1273.9	0.003782	0.003771	— 0.3
1273.4	0.003803	0.003770	— 0.9
1567.2	0.004656	0.004684	+ 0.6
1527.9	0.004545	0.004561	+ 0.4
			0.4 Ave.



TABLE VI.

*Plasticity of a Paint Consisting of 50 per cent. Lithopone by Weight and 50 per cent. of Linseed Oil.*

$$\begin{aligned} f &= 35.5 \\ \mu &= 0.930 \\ \rho &= 1.5225 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000003440 \text{ F} - 0.0001222$$

Shearing Stress --Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
618.2	0.002015	0.002004	— 0.6
617.5	0.002000	0.002002	+ 0.1
808.1	0.002657	0.002658	+ 0.1
805.9	0.002643	0.002650	+ 0.3
982.0	0.003224	0.003256	+ 1.0
981.0	0.003250	0.003253	+ 0.1
1187.6	0.003981	0.003963	— 0.4
1185.1	0.003972	0.003955	— 0.4
			0.4 Ave.

TABLE VII.

*Plasticity of a Paint Consisting of 45 per cent. Lithopone by Weight and 55 per cent. Linseed Oil.*

$$\begin{aligned} f &= 18.25 \\ \mu &= 1.108 \\ \rho &= 1.428 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000003834 \text{ F} - 0.0000700$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
377.2	0.001380	0.001377	— 0.2
377.5	0.001368	0.001376	+ 0.6
377.0	0.001367	0.001375	+ 0.6
879.5	0.003321	0.003304	— 0.5
879.2	0.003284	0.003302	+ 0.6
1296.6	0.004916	0.004905	— 0.2
1296.4	0.004907	0.004904	— 0.1
1482.2	0.005652	0.005613	— 0.7
1480.3	0.005656	0.005610	— 0.8
1656.4	0.006221	0.006286	+ 1.0
1659.7	0.006307	0.006298	— 0.1
1855.5	0.007030	0.007050	+ 0.3
1854.2	0.007036	0.007045	+ 0.1
			0.4 Ave.



TABLE VIII.

*Plasticity of a Paint Consisting of 40 per cent. Lithopone by Weight and 60 per cent. of Linseed Oil.*

$$\begin{aligned} f &= 8.83 \\ \mu &= 1.283 \\ \rho &= 1.347 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000004188 F - 0.0000370$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
1876.6	0.007835	0.007823	— 0.2
1876.2	0.007821	0.007803	— 0.2
1519.3	0.006327	0.006326	0.0
1518.7	0.006306	0.006324	+ 0.3
1142.7	0.004732	0.004749	+ 0.4
1142.4	0.004728	0.004748	+ 0.4
764.7	0.003153	0.003166	+ 0.4
768.1	0.003160	0.003180	+ 0.6
431.1	0.001783	0.001769	— 0.8
419.2	0.001711	0.001719	+ 0.5
423.0	0.001761	0.001735	— 1.5
			0.5 Ave.

TABLE IX.

*Plasticity of a Paint Consisting of 35 per cent. Lithopone by Weight and 65 per cent. of Linseed Oil.*

$$\begin{aligned} f &= 7.68 \\ \mu &= 1.405 \\ \rho &= 1.277 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000004347 F - 0.00003338$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
377.6	0.001612	0.001629	+ 1.0
381.3	0.001629	0.001645	+ 1.0
681.2	0.002903	0.002939	+ 1.2
680.8	0.002908	0.002937	+ 1.0
927.2	0.004032	0.003999	— 0.8
926.6	0.003996	0.003997	0.0
1205.4	0.005198	0.005199	0.0
1204.7	0.005186	0.005196	+ 0.2
1725.6	0.007642	0.007443	— 2.7
1730.1	0.007648	0.007463	— 2.5
			1.0 Ave.



TABLE X.

*Plasticity of a Paint Consisting of 25 per cent. Lithopone by Weight and 75 per cent. of Linseed Oil.*

$$\begin{aligned} f &= 2.5 \\ \mu &= 1.738 \\ \rho &= 1.1535 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000004860 \text{ F} - 0.00001221$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
324.1	0.001568	0.001571	+ 0.2
321.7	0.001572	0.001560	— 0.8
465.8	0.002263	0.002258	— 0.2
473.4	0.002246	0.002295	+ 2.2
823.6	0.003986	0.003992	+ 0.2
823.1	0.003997	0.003990	— 0.2
1194.6	0.005796	0.005791	— 0.1
1194.1	0.005795	0.005788	— 0.1
1482.2	0.007209	0.007185	— 0.3
1481.6	0.007183	0.007182	0.0
1748.6	0.008500	0.008476	— 0.3
1747.7	0.008446	0.008472	+ 0.3
			0.4 Ave.

TABLE XI.

*Plasticity of a Paint Consisting of 15 per cent. Lithopone by Weight and 85 per cent. of Linseed Oil.*

$$\begin{aligned} f &= 3.1 \\ \mu &= 2.029 \\ \rho &= 1.049 \\ t &= 25^\circ \end{aligned}$$

$$M/t = 0.000005155 \text{ F} - 0.0000159$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
366.7	0.001876	0.001875	0.0
364.5	0.001865	0.001863	— 0.1
710.8	0.003648	0.003649	0.0
716.4	0.003658	0.003678	+ 0.6
1093.5	0.005623	0.005622	0.0
1096.8	0.005632	0.005639	+ 0.1
1490.0	0.007649	0.007666	+ 0.2
1490.3	0.007659	0.007667	+ 0.1
2069.5	0.01060	0.01065	+ 0.5
2005.4	0.01041	0.01032	— 0.9
			0.2 Ave.



TABLE XII.

*Fluidity of Linseed Oil.*

$$f=0.0$$

$$\varphi=2.423$$

$$\rho=0.9259$$

$$t=25^{\circ}$$

$$M/t=0.000005436 \text{ F}$$

Shearing Stress —Dynes per cm. <sup>2</sup>	Efflux in g. per second—Observed.	Efflux in g. per second—Calculated.	Percentage Deviation.
1549.4	0.00839	0.00842	+ 0.3
1562.1	0.00851	0.00849	— 0.2
836.2	0.00652	0.00650	— 0.3
831.8	0.00647	0.00645	— 0.3
1196.2	0.004552	0.004546	— 0.1
1187.1	0.004520	0.004522	0.0
586.5	0.003174	0.003188	+ 0.4
580.5	0.003144	0.003156	+ 0.4
264.1	0.001435	0.001436	+ 0.1
256.2	0.001389	0.001393	+ 0.3

0.2 Ave.

TABLE XIII.

*Summary of Plasticity Data.*

Percentage Lithopone		Density		Yield Value		Mobility	
by wt.	by vol.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
65	28.6	1.885	1.888	128.9	128.9	0.441	0.459
62.5	26.4	1.815	1.815	114.5	113.7	0.526	0.537
60	24.4	1.747	1.748	107.6	98.6	0.617	0.616
55	20.8	1.630	1.627	61.5	68.2	0.788	0.773
50	17.7	1.5225	1.522	35.5	37.9	0.930	0.930
45	15.0	1.428	1.430	18.2	7.6	1.108	1.087
40	12.6	1.347	1.348	8.8	0.0	1.283	1.244
35	10.4	1.277	1.275	7.7	0.0	1.405	1.401
25	4.2	1.1535	1.151	2.5	0.0	1.738	1.715
15	2.8	1.049	1.048	3.1	0.0	2.029	2.029
0	0.0	0.9259	. . . .	0.0	0.0	2.423	2.500

## DISCUSSION OF RESULTS.

*The Density.*—We have calculated the densities of the mixtures on the assumption that there is neither expansion nor contraction in volume on mixing. The formula used is

$$\rho = \frac{1}{mv_1 + nv_2}$$

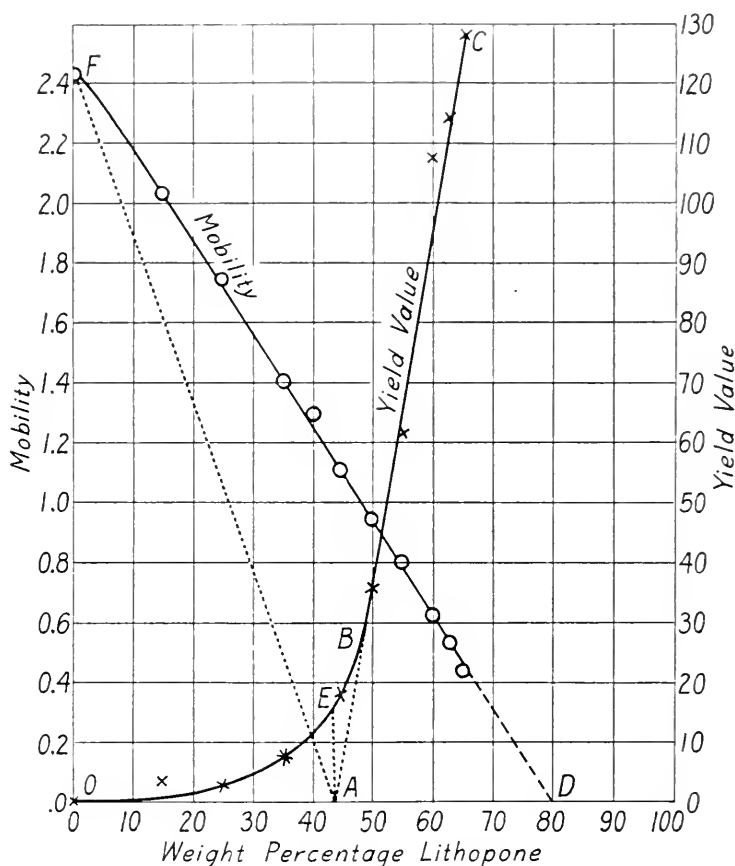
where  $m$  is the fraction linseed oil of specific volume 1.080 and  $n$  is the fraction of lithopone of specific volume 0.2326. The calcu-



lated values given in the fourth column of Table XIII are in very good agreement with the observed value.

*The Yield Value.*—The yield values are a linear function of the weight (or volume) concentration, for concentrations over about 43 per cent. by weight, or 14 per cent. by volume, corresponding to the point *A* in Fig. 1. The equation of the curve is

FIG. 1.



The variation in the yield value and mobility obtained by dilution of a suspension of lithopone in linseed oil with more linseed oil at 25° C.

$f = 606.8 n - 265.5$ . The calculated values are given in the sixth column of Table XIII. This is similar to the relationship already found for clay suspensions.

According to earlier work<sup>5</sup> the point *A* is the concentration which sharply demarcates the solid from the liquid, the curve *FA* in the figure representing the fluidity curve which we would obtain with a very small shearing stress.

As a matter of fact every concentration with which we worked showed a measurable yield value, hence we have obtained a yield

<sup>5</sup> "Fluidity and Plasticity," p. 202.



value curve for concentrations below 43 per cent. by weight (14 per cent. by volume) *OE*, which very much resembles the yield value concentration curve given for solutions of nitrocellulose in the preceding paper. The question immediately presents itself whether even in nitrocellulose solutions the yield value concentration curve would not become linear at higher concentrations.

The reason why Kleinspehn failed to get true fluidities is because the solid particles suspended in the oil made the material no longer flow as a true fluid, so that he was working in a mixed regime, and some sort of plasticity correction was imperative. It has already been explained<sup>6</sup> why solid particles suspended in a liquid cause a loss of energy during shear that is not found in true fluids.

This plasticity correction finds its analogue in the viscosity correction which it is sometimes necessary to make in measurements of plasticity on account of seepage or slippage.

Had Kleinspehn determined all of his fluidities with a small shearing stress indicated by the yield value of the point *E* in the figure, he would have obtained the curve *FA* and the true concentration for the theoretical zero yield value. Had he used a smaller shearing stress the curve found would have been to the left of *FA*, and had he used a very large shearing stress, it would have approached the curve *FD*, which we obtained.

*The Mobility.*—The mobility turns out to be a linear function of the weight concentration. The curve is represented by the equation

$$\mu = 2.5 - 3.14n$$

and the calculated values are given in the last column of Table XIII. It appears that the mobility curve merges without discontinuity into the fluidity curve; in fact, the mobility curve may be regarded as the fluidity curve when the apparent fluidities are measured at very high shearing stresses.

The fluidity of linseed oil does not lie exactly on the mobility curve. The value was redetermined to prove that it was not an experimental error.

A zero of mobility seems to be clearly indicated at a concentration of 79.6 per cent. by weight, or 45.6 per cent. by volume.

---

<sup>6</sup> "Fluidity and Plasticity," p. 200.



It was predicted that there would be zero of mobility when there was close packing of the particles. For spheres of equal size, cubical close-packing would correspond to a concentration of 52.4 per cent. by volume. But of course we cannot assume that the particles of lithopone are equal spheres.

*The Effect of Temperature on the Plasticity.*—In Tables III and IV we have a little further evidence<sup>7</sup> of the effect of temperature, the yield value increasing from 128.1 to 145.5 and the mobility decreasing from 0.4412 to 0.3686 as the temperature is lowered from 25 to 20° C. The fluidity of linseed oil, according to Hyden, is 2.08 at 20° and 2.52 at 25°, hence the increase is 19.3 per cent. of the mean. The increase in the mobility is 19.5 per cent., which proves that the increase in mobility is entirely due to the increase in fluidity of the medium.

#### CONCLUSIONS.

1. From the foregoing it appears that suspensions, as well as the emulsoid type of colloids, show the properties of plastic materials even at very low concentrations of the disperse phase. The viscosity, as ordinarily measured, is not a constant but a function of the shearing stress.

2. At high concentrations, the yield value concentration relation is linear; the material is truly plastic.

3. At lower concentrations, the yield value concentration relation is not linear; the material may be said to be pseudo-plastic.

4. It seems to be possible to distinguish sharply between the plastic and the pseudo-plastic condition. With lithopone suspended in linseed oil, the transition occurs in a mixture containing 14 per cent. of lithopone by volume. This concentration may be related to important properties of the material, such as the fineness of structure, adhesion between the particles *et cet.*

5. The mobility-concentration (by weight) curve is linear, hence it seems possible by measuring the plasticity of a paint and of one other paint obtained from the first by thinning to predict the plasticity of any paint made by thinning, provided that we neglect the plasticity correction for the pseudo-plastic paints.

6. At 45.6 per cent. by volume of lithopone, the mobility would have a zero value. This concentration of zero mobility seems to be simply connected with the pore space of the material,

---

<sup>7</sup> "Fluidity and Plasticity," p. 230.



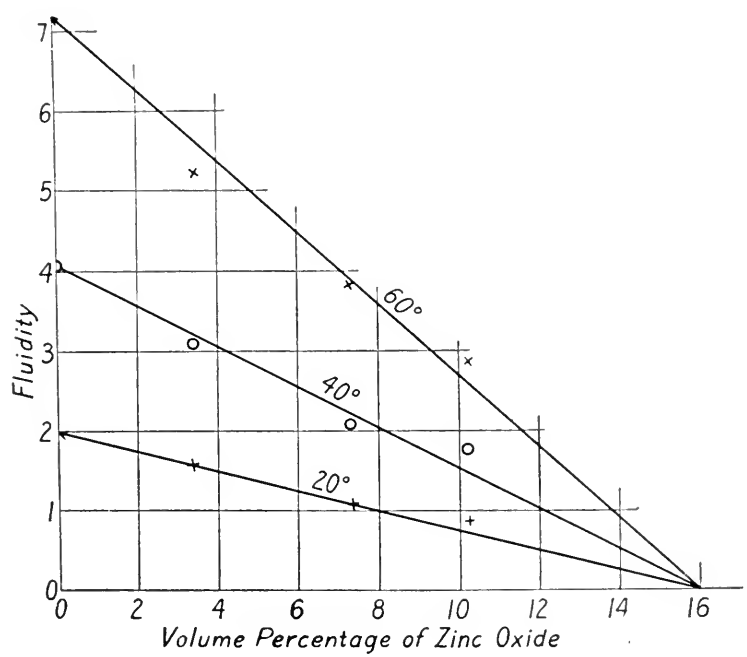
and it may have considerable significance in determining the flow of dispersions.

We desire to thank the E. I. du Pont de Nemours and Company for their interest and support which have made possible this investigation.

APPENDIX.

Mr. W. G. Kleinspehn, while working with one of the authors, endeavored to find the concentration corresponding to zero fluidity following the method which had been employed by Bingham and Durham.<sup>8</sup> The effort, however, was unsuccessful, for the

FIG. 2.



The apparent fluidities of suspensions of zinc oxide in linseed oil at 20°, 40°, 60°, measured by W. G. Kleinspehn.

curves from the apparent fluidities were not linear and they could not be extrapolated to zero fluidity. We believe that the difficulty was due to the relatively high viscosity of linseed oil which necessitated using a viscometer with a much wider capillary than was used by Bingham and Durham. As the paint became thicker at the higher concentrations, higher shearing stresses were necessary, which we believe tended to increase the apparent fluidity

<sup>8</sup> Amer. Chem. J., 46, 278 (1911).



obtained. Some of the results are given in Table XIV and in Fig. 2, and in the last column values calculated by the formula<sup>9</sup>

$$\varphi = \left(1 - \frac{b}{c}\right) \varphi_1$$

are given, where  $b$  is the percentage of Florence zinc oxide and  $c$  is a constant 0.16 which should represent the concentration of zero fluidity and  $\varphi_1$  is the fluidity of the oil. There is poor concordance, particularly at the higher concentrations.

TABLE XIV.

*The Apparent Fluidities of Suspensions of Florence Zinc Oxide in Linseed Oil as Measured in the Viscometer by W. G. Kleinspehn.*

Percentage of of Pigment by Volume.	Temp.	Time— Seconds.	Pressure g. per cm. <sup>2</sup>	Density t/4°.	Fluidity Observed.	Fluidity Calculated.
0.0	20°	505.3	124.7	0.9306	2.013	2.013
0.0	40°	407.3	75.7	0.9173	4.116	4.116
0.0	60°	484.5	36.5	0.9041	7.17	7.17
3.42	20°	345.0	233.3	1.097	1.576	1.58
3.42	40°	472.1	87.2	1.082	3.08	3.24
3.42	60°	423.0	57.3	1.069	5.24	5.64
7.32	20°	502.0	233.0	1.280	1.085	1.09
7.32	40°	545.8	111.1	1.264	2.093	2.23
7.32	60°	467.0	71.3	1.249	3.81	3.89
10.18	20°	491.4	293.3	1.463	0.594	0.73
10.18	40°	379.0	189.9	1.438	1.763	1.50
10.18	60°	486.5	90.7	1.422	2.874	2.61

Under the impression that the above values could not possibly represent true fluidities, Mr. Kleinspehn in 1919 went so far as to measure the apparent fluidity of the 10.18 per cent. paint at 20° C. at different pressures, and obtained fluidities given in Table XV which show a steady increase as the pressure was raised of some 10 per cent., the pressure increasing from 206 to 510 g. per cm.<sup>2</sup> At the time no means were at hand for getting around the difficulty. By plotting the volume of flow against the shearing stress the difficulty now disappears at once. We see that the linear equation

$$V/t = 0.00002568 F - 0.000824$$

reproduces perfectly all of the data. When the flow is zero the shearing stress is still 321 dynes per cm.,<sup>2</sup> which is evidently the yield value of the material. So whereas the apparent fluidity

<sup>9</sup> "Fluidity and Plasticity," p. 203.



varied widely, this is because the paint had a very pronounced yield value, and when this is taken into account, the mobility, which is proportional to the slope of the above curve, becomes constant.

TABLE XV.

*The Effect of Using Different Pressures upon the Apparent Fluidity of a 10.18 per cent. Suspension of Zinc Oxide by Volume in Linseed Oil at 20° C.*

Time seconds.	Pressure g. per cm. <sup>2</sup>	Shearing Stress Dynes per cm. <sup>2</sup>	Apparent Fluidity.	Rate of Flow ml. per sec. Observed.	Rate of Flow Calculated.
768	206	235	0.802	0.00521	0.00521
527	288	328	0.836	0.00759	0.00761
436	340	388	0.856	0.00917	0.00915
350	418	477	0.869	0.01143	0.01143
283	510	582	0.879	0.01413	0.01413

**Boric Acid as a Preservative for Canned Goods.**—In principle the sterilization of foods in the canning process should be sufficient for preserving them for a reasonable time, but in practise, especially in large-scale operation, incomplete sterilization may occur and unwholesome conditions develop. One phenomenon frequently seen in spoiled canned goods is swelling of the container on account of the production of gas. These “swells,” as they are called, are sometimes opened by a small perforation which allows the escape of the gas, resealed, relabelled and turned back into the market, but these practises are now probably not common. Many inquiries have been made of the Bureau of Chemistry concerning the use of boric acid as an aid in preservation. In earlier years, salicylic acid was largely used by housekeepers in home canning, though the nature of the substance was not generally known. The legislation against this has necessitated resort to other preservatives, and sodium benzoate and boric acid have been brought into notice. The Bureau of Chemistry has made a careful investigation of the action of boric acid on the organisms commonly associated with spoiled food, and also made analyses of boric acid preparations offered in the market. The work was done and the report prepared by Ruth T. Edmondson, Charles Thom and I. T. Giltner. The analyses of the powders were made by J. I. Palmore. They are sold in packages which are apparently intended to contain an ounce, but considerable difference was found in the net boric acid content of the several samples. The directions gave no warning that an excess of the material in the food might be harmful. The experiments are given fully and in detail. The results are mainly: Boric acid canning powders as sold, when used in the amount directed, con-



trol the growth of certain molds and aerobic microörganisms, but these are not responsible for spoilage in processed material. The powders had no appreciable effect on the growth of *B. botulinus*, which is a very serious contamination in some foods. The use of the powders is wasteful, since careful processing will fully preserve the materials for a reasonable time. In dealing with the moderately neutral vegetables, the use of the powder, with the inadequate heating recommended and likely to be used by the home canner, will not control the growth of the *B. botulinus*. H. L.

**New Method of Helium Recovery.** (*Am. Chem. Soc. News Service.*)—Satisfactory operation on a laboratory scale of a simplified and much cheaper method of recovering helium is reported through the American Chemical Society by H. Foster Bain, Director of the U. S. Bureau of Mines. In a test-run made within the last month at the cryogenic laboratory in the Interior Department Building, helium was recovered from natural gas in one operation in sufficient purity for use in dirigibles or balloons. "This development," Mr. Bain said, "indicates that very soon commercial production of helium for lighter-than-air craft may be feasible." Not only will this insure safety from fire and explosions, but it is almost certain to result in an entirely new type of airship design. The motor, for instance, could be placed inside the envelope of a helium ship if necessary. The research work leading up to this achievement was directed by the United States Helium Board, composed of Lieutenant Commander F. M. Kraus, representing the Navy; Colonel R. F. Fravel, representing the Army; Dr. R. B. Moore, chief chemist of the U. S. Bureau of Mines, and H. S. Mulliken, production engineer, alternate. The actual work of development was directed by the Board of Helium Engineers, with the following membership: M. H. Roberts, Franklin Railway Supply Company; R. C. Tolman, of the California Institute of Technology; W. L. DeBaufre, University of Nebraska; Edgar Buckingham, of the U. S. Bureau of Standards, and John W. Davis, of the U. S. Bureau of Mines. The government also had the assistance of Dr. Frederick Keyes, Massachusetts Institute of Technology, and Dr. Harvey N. Davis, Harvard.

Helium recovery, as carried on at government plants in Texas, results in a gas of about 64 per cent. purity, and necessitates a second operation to remove impurities. By the old method the flow from the natural gas wells is directed through a series of compressors which reduce the various gases in the mixture to liquid form. Methane (illuminating gas) becoming liquid at a higher temperature is taken off first. The remaining gases are then, one by one, liquefied, and helium, having an exceedingly low liquefying point, remains. The difficulty with the old method is to liquefy all of the nitrogen in the mixture.



# APPLICATIONS OF HEAVISIDE EXPANSION THEOREM.\*

BY

LOUIS COHEN, Ph.D.

Consulting Engineer, Signal Corps, U.S.A.

It was suggested to me that a few illustrations worked out in detail, showing the application of the Expansion Theorem in the solution of problems, would be helpful to bring about a better appreciation of the general utility of the theorem as a practical method for the solution of electrical problems. Acting on this suggestion, which I believe to be good, I have worked out a few examples relating to somewhat different branches of electrical engineering in order to show the wide range of applicability of the theorem.

In my paper on the derivation of the Expansion Theorem Formulæ<sup>1</sup> I have given two formulæ, one for constant e.m.f. and the other for sinusoidal e.m.f. as follows:

Constant e.m.f. :

$$I = \frac{E}{Z(p)_{p=0}} + \sum_1^m \frac{E \varepsilon^{p_n t}}{p_n \frac{\partial Z(p)}{\partial p} \big|_{p=p_n}} \quad (1)$$

Sinusoidal e.m.f. :

$$I = \frac{E \varepsilon^{j\omega t}}{Z(p)_{p=j\omega}} - \sum_1^m \frac{E \varepsilon^{p_n t}}{(j\omega - p_n) \frac{\partial Z(p)}{\partial p} \big|_{p=p_n}} \quad (2)$$

In the second formula the real part only to be used.

Formula (2) is more general, it includes (1); putting  $\omega = 0$  in (2) it reduces to (1).

In applying the above formulæ to the solution of problems, we may either transform the formula in any particular case to give it a form which is more or less known as derived by other methods, or what is simpler, and in some cases the only practical method, to use the formulæ directly in the form given by (1)

\* Communicated by General George O. Squier, Chief Signal Officer, U.S.A., and Associate Editor of this JOURNAL.

<sup>1</sup> JOUR. FRANK. INST., Vol. 194, No. 6, Dec., 1922.



or (2) for numerical calculations. We shall give here illustrations of both methods.

#### PROBLEM 1.

Circuit of inductance  $L$  and resistance  $R$  sinusoidal e.m.f. impressed on circuit, determine the current at any time  $t$  after the e.m.f. is applied.

The circuit equation is

$$L \frac{dI}{dt} + RI = E\varepsilon^{j\omega t}, \quad (3)$$

and

$$I = \frac{E\varepsilon^{j\omega t}}{Lp + R}. \quad (4)$$

In this case

$$Z(p) = Lp + R, \quad (5)$$

a one-degree equation

$$\text{for } Z(p) = 0,$$

$$p = -\frac{R}{L}, \quad (6)$$

$$\frac{\partial Z(p)}{\partial p} = L.$$

Substituting in (2),

$$\begin{aligned} I &= \frac{E\varepsilon^{j\omega t}}{Lj\omega + R} - \frac{E\varepsilon^{-\frac{R}{L}t}}{\left(j\omega + \frac{R}{L}\right)L}, \\ &= \frac{E}{Lj\omega + R} \left\{ \varepsilon^{j\omega t} - \varepsilon^{-\frac{R}{L}t} \right\}. \end{aligned} \quad (7)$$

The real part of above equation is

$$\begin{aligned} I &= \frac{E}{\sqrt{R^2 + L^2\omega^2}} \cos(\omega t - \varphi) - \frac{ER}{R^2 + L^2\omega^2} \varepsilon^{-\frac{R}{L}t}, \\ \text{tau } \varphi &= \frac{L\omega}{R}. \end{aligned} \quad (8)$$

When  $\omega = 0$ , constant e.m.f. the above reduces to

$$I = \frac{E}{R} \left\{ 1 - \varepsilon^{-\frac{R}{L}t} \right\}. \quad (9)$$

Formulae (8) and (9) are the well-known expressions for the current rise in an inductive circuit.



PROBLEM 2.

Resistance, inductance and capacity ( $R, L, C$ ) in circuit sinusoidal e.m.f. impressed.

Circuit equation:

$$L \frac{dI}{dt} + RI + \frac{1}{C} \int I dt = E \epsilon^{j\omega t} \quad (10)$$

or

$$\begin{aligned} \left( Lp + R + \frac{1}{Cp} \right) I &= E \epsilon^{j\omega t} \\ I &= \frac{E \epsilon^{j\omega t}}{Lp + R + \frac{1}{Cp}}. \end{aligned} \quad (11)$$

In this case

$$Z(p) = \frac{LCp^2 + RCp + 1}{Cp}, \quad (12)$$

a second-degree equation.

The roots of the above equation are

$$\begin{aligned} p_1 &= -\alpha + j\beta, \\ p_2 &= -\alpha - j\beta, \end{aligned} \quad \left. \vphantom{\begin{aligned} p_1 &= -\alpha + j\beta, \\ p_2 &= -\alpha - j\beta, \end{aligned}} \right\} \quad (13)$$

where

$$\alpha = \frac{R}{2L}, \quad \beta = \sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}. \quad (14)$$

$$\frac{\partial Z(p)}{\partial p} = L - \frac{1}{Cp^2}. \quad (15)$$

Substituting for  $p$  in (15) the values  $p_1$  and  $p_2$  as given by (13) we obtain

$$\left. \begin{aligned} \frac{\partial Z(p)}{\partial p} p = p_1 &= \frac{2L\beta}{\beta + j\alpha}, \\ \frac{\partial Z(p)}{\partial p} p = p_2 &= \frac{2L\beta}{\beta - j\alpha}. \end{aligned} \right\} \quad (16)$$

Substituting the above values in (2), we get the expression for the current in the circuit as follows:

$$I = \frac{E \epsilon^{j\omega t}}{Lj\omega + R + \frac{1}{Cj\omega}} - \frac{E \epsilon^{-(\alpha - j\beta)t}}{(j\omega + \alpha - j\beta) \frac{2L\beta}{\beta + j\alpha}} - \frac{E \epsilon^{-(\alpha + j\beta)t}}{(j\omega + j\beta - \alpha) \frac{2L\beta}{\beta - j\alpha}}. \quad (17)$$



The first term in above expression represents the steady state, periodic component, and the other two terms the transient current component. Combining the two terms of the transient current component, we get

$$I_t = \frac{E\varepsilon^{-\alpha t}}{2L\beta} \left\{ \frac{\beta + j\alpha}{j\omega - j\beta + \alpha} \varepsilon^{j\beta t} + \frac{\beta - j\alpha}{j\omega + j\beta + \alpha} \varepsilon^{-j\beta t} \right\} \\ = \frac{E\varepsilon^{-\alpha t}}{2L\beta} \left\{ \frac{(j\beta\omega + j\beta^2 - \omega\alpha + j\alpha^2) \varepsilon^{j\beta t} + (j\beta\omega - j\beta^2 + \omega\alpha - j\alpha^2) \varepsilon^{-j\beta t}}{\beta^2 + \alpha^2 - \omega^2 + 2j\omega\alpha} \right\}. \quad (18)$$

Replacing

$$\varepsilon^{\pm j\beta t} \text{ by } \cos \beta t \pm j \sin \beta t,$$

the above will reduce to

$$I_t = \frac{E\varepsilon^{-\alpha t}}{L\beta} \left\{ \frac{j\beta\omega \cos \beta t - (\beta^2 + \alpha^2 + j\omega\alpha) \sin \beta t}{\beta^2 + \alpha^2 - \omega^2 + 2j\omega\alpha} \right\}. \quad (19)$$

The real part of equation (19) is

$$I_t = \frac{E\varepsilon^{-\alpha t}}{L\beta} \left\{ \frac{2\alpha\beta\omega^2 \cos \beta t - ((\alpha^2 + \beta^2)^2 + \omega^2(\alpha^2 - \beta^2)) \sin \beta t}{(\beta^2 + \alpha^2 - \omega^2)^2 + 4\alpha^2\omega^2} \right\}. \quad (20)$$

The above may be put in a simpler form

$$I_t = \frac{E\varepsilon^{-\alpha t}}{L\beta} \frac{(\alpha^2 + \beta^2) \cos(\beta t + \psi)}{\sqrt{(\beta^2 + \alpha^2 - \omega^2)^2 + 4\alpha^2\omega^2}}, \quad (21) \\ \tan \psi = \frac{(\alpha^2 + \beta^2)^2 + \omega^2(\alpha^2 - \beta^2)}{2\alpha\beta\omega^2}.$$

Taking the real part of the first term of the right-hand member of (17) and combining with (20), we have the complete expression for the current:

$$I = \frac{E \cos(\omega t - \varphi)}{\sqrt{\left(L\omega - \frac{1}{C\omega}\right)^2 + R^2}} - \frac{E\varepsilon^{-\alpha t}}{L\beta} \frac{(\alpha^2 + \beta^2) \cos(\beta t + \psi)}{\sqrt{(\beta^2 + \alpha^2 - \omega^2)^2 + 4\alpha^2\omega^2}} \quad (22)$$

Putting  $C = \infty$  short-circuiting condenser, we have  $\beta = j\alpha$  and equation (20) reduces to

$$I_t = \frac{ER\varepsilon^{-\frac{R}{L}t}}{R^2 + L^2\omega^2},$$

the same as the second term of right-hand member of equation (8).



## PROBLEM 3.

Coupled circuits—two inductive circuits electromagnetically coupled. The circuit equations are:

$$\left. \begin{aligned} (L_1 p + R_1) I_1 + M p I_2 &= E \epsilon^{j\omega t}, \\ (L_2 p + R_2) I_2 + M p I_1 &= 0. \end{aligned} \right\} \quad (23)$$

Solving for  $I_1$  and  $I_2$  we have

$$\left. \begin{aligned} I_1 &= \frac{E (L_2 p + R_2) \epsilon^{j\omega t}}{(L_1 L_2 - M^2) p^2 + (R_1 L_2 + R_2 L_1) p + R_1 R_2}, \\ I_2 &= \frac{-E M p \epsilon^{j\omega t}}{(L_1 L_2 - M^2) p^2 + (R_1 L_2 + R_2 L_1) p + R_1 R_2}. \end{aligned} \right\} \quad (24)$$

For the primary circuit

$$Z(p) = \frac{(L_1 L_2 - M^2) p^2 + (R_1 L_2 + R_2 L_1) p + R_1 R_2}{L_2 p + R_2}. \quad (25)$$

For the secondary circuit

$$Z(p) = - \frac{(L_1 L_2 - M^2) p^2 + (R_1 L_2 + R_2 L_1) p + R_1 R_2}{M p}. \quad (26)$$

The roots of the equation  $Z(p) = 0$  are the same for (25) and (26).

$$\left. \begin{aligned} p_1 &= \frac{-(R_1 L_2 + R_2 L_1) + \sqrt{(R_1 L_2 - R_2 L_1)^2 + 4 R_1 R_2 M^2}}{2 (L_1 L_2 - M^2)}, \\ p_2 &= \frac{-(R_1 L_2 + R_2 L_1) - \sqrt{(R_1 L_2 - R_2 L_1)^2 + 4 R_1 R_2 M^2}}{2 (L_1 L_2 - M^2)}. \end{aligned} \right\} \quad (27)$$

Equations (27) may be put in the following form:

$$\left. \begin{aligned} p_1 \\ p_2 \end{aligned} \right\} = \frac{-(\alpha_1 + \alpha_2) \pm \sqrt{(\alpha_1 - \alpha_2)^2 + 4 \alpha_1 \alpha_2 K^2}}{1 - K^2} \quad (28)$$

$$\alpha_1 = \frac{R_1}{2 L_1}, \quad \alpha_2 = \frac{R_2}{2 L_2}, \quad K^2 = \frac{M^2}{L_1 L_2}. \quad (29)$$

By (25)

$$Z(p) = L_1 \left\{ \frac{(1 - K^2) p^2 + 2 (\alpha_1 + \alpha_2) p + 4 \alpha_1 \alpha_2}{p + 2 \alpha_2} \right\} \quad (30)$$

and

$$\frac{\partial Z(p)}{\partial p} = L_1 \left\{ \frac{(1 - K^2) (p^2 + 4 \alpha_2 p) + 4 \alpha_2^2}{(p + 2 \alpha_2)^2} \right\}. \quad (31)$$

We may now substitute the values of  $p_1$ ,  $p_2$ , and  $\frac{\partial Z(p)}{\partial p}$  given by (28) and (31) in (2) and transform the formula into a form corresponding to the typical forms for problems of this



kind given in text-books. It is just as simple, however, if not simpler, to use formulæ (30), (31) and (2) in the present form for numerical calculations. After all, the principal value of a formula is its use for numerical computations and formula (2) is just as convenient for the purpose.

Example:

$$L_1 = 0.1 \text{ henry, } R_1 = 10 \text{ ohms, } L_2 = 0.2 \text{ henry, } R_2 = 25 \text{ ohms,}$$

$$M = 0.1 \text{ henry, } \omega = 2\pi \times 60 = 377, E = 100 \text{ volts.}$$

$$\alpha_1 = 50, \alpha_2 = 62.5, K^2 = 0.5$$

$$p_1 = -64.9, p_2 = -385$$

$$\frac{\partial Z(p)}{\partial p} p = p_1 = 0.2664, \frac{\partial Z(p)}{\partial p} p = p_2 = 0.0615$$

$$Z(p)_{p=j\omega} = \frac{-1161 + j1697}{25 + j75.4} = 15.7 + j20.6.$$

Substituting these values in (2)

$$I_1 = \frac{100 \varepsilon^{j\omega t}}{15.7 + j20.6} - \frac{100 \varepsilon^{-64.9t}}{(j377 + 64.9) \times 0.2664} - \frac{100 \varepsilon^{-385t}}{(j377 + 385) \times 0.0615}.$$

The real part

$$I_1 = 3.86 \cos(\omega t - \varphi) - 0.166 \varepsilon^{-64.9t} - 2.16 \varepsilon^{-385t} \text{ amperes.}$$

For constant e.m.f.

$$\begin{aligned} I_1 &= \frac{100}{10} - \frac{100 \varepsilon^{-64.9t}}{64.9 \times 0.2664} - \frac{100 \varepsilon^{-385t}}{385 \times 0.0615} \\ &= 10 - 5.77 \varepsilon^{-64.9t} - 4.23 \varepsilon^{-385t} \text{ amperes.} \end{aligned}$$

The results for constant e.m.f. check with those obtained by a different method given as an example in my book "Calculations of Alternating Currents Problems," page 193.

To calculate the value of the current in the secondary circuit, we have by (26)

$$\begin{aligned} Z(p) &= \frac{(L_1 L_2 - M^2)p^2 + (R_1 L_2 + R_2 L_1)p + R_1 R_2}{M p} \\ \frac{\partial Z(p)}{\partial p} &= \frac{M\{(1 - K^2)p^2 - 4\alpha_1 \alpha_2\}}{K^2 p^2} \end{aligned} \quad (32)$$

The values of  $p_1$  and  $p_2$  are the same as before given by (29), which combined with (32) and (2) is all the data necessary for numerical calculations.



PROBLEM 4.

The transient voltage and current on a line of distributed inductance capacity and resistance. We have for this case the well-known equation of propagation.

$$\frac{d^2 V}{dx^2} = q^2 V, \quad (33)$$

$$q^2 = Cp(Lp + R). \quad (34)$$

The solution of (33) is

$$V = A\epsilon^{qx} + B\epsilon^{-qx}. \quad (35)$$

The expression for the current at any point on the line can be readily obtained from the voltage current relation

$$(Lp + R)I = -\frac{dV}{dx},$$

and

$$I = \frac{-q}{Lp + R} \{A\epsilon^{qx} - B\epsilon^{-qx}\}. \quad (36)$$

Assume an e.m.f.  $E\epsilon^{j\omega t}$  impressed at one end of the line and the other end grounded, the terminal conditions in this case are :

$$\left. \begin{array}{l} x = 0, V = E\epsilon^{j\omega t} \\ x = l, V = 0 \end{array} \right\} \quad (37)$$

The constants  $A$  and  $B$  of equation (35) are determined by (37) and substituting these values in (36) we obtain the expression for the current on the line,

$$\begin{aligned} I &= \frac{q}{Lp + R} \frac{E\{\epsilon^{q(l-x)} + \epsilon^{-q(l-x)}\}}{\epsilon^{ql} - \epsilon^{-ql}} \epsilon^{j\omega t} \\ &= \frac{E \cosh q(l-x)}{(Lp + R) \sinh ql} \cdot \frac{1}{q} \end{aligned} \quad (38)$$

The generalized impedance in this case is

$$Z(p) = \frac{Lp + R}{q} \frac{\sinh ql}{\cosh q(l-x)}. \quad (39)$$

The values of  $q_m$  and  $p_m$  are determined from the equation  $Z(p) = 0$ , which in this case gives

$$\left. \begin{array}{l} \sinh ql = 0 \\ ql = jn\pi, \quad n = 0, 1, 2, 3, \dots \\ q^2 = Cp(Lp + R) = -\frac{n^2\pi^2}{l^2} \end{array} \right\} \quad (40)$$



Hence

$$\left. \begin{aligned} p_n &= -\frac{R}{2L} \pm \sqrt{\frac{R^2}{4L^2} - \frac{n^2\pi^2}{l^2LC}}, \\ &= -\alpha \pm j\beta_n, \end{aligned} \right\} \quad (41)$$

where

$$\left. \begin{aligned} \alpha &= -\frac{R}{2L}, \\ \beta_n &= \sqrt{\frac{n^2\pi^2}{LCl^2} - \alpha^2}. \end{aligned} \right\} \quad (42)$$

The expression for  $\frac{\partial Z(p)}{\partial p}$ , for  $\text{Sinh } ql = 0$ , is readily obtained from (39) as follows:

$$\left. \begin{aligned} \frac{\partial Z(p)}{\partial p} &= \frac{l(Lp + R)}{q \text{Cosh } qx} \frac{\partial q}{\partial p}, \\ \frac{\partial q}{\partial p} &= \frac{p + \alpha}{qv^2}, \left( v^2 = \frac{1}{LC} \right) \end{aligned} \right\} \quad (43)$$

hence

$$\frac{\partial Z(p_m)}{\partial p_m} = \frac{(R + Lp_m) l (p_m + \alpha)}{q_m^2 v^2 \text{Cosh } q_m x}. \quad (44)$$

The above may be put in the following form:

$$\frac{\partial Z(p_m)}{\partial p_m} = \frac{j l \sqrt{\frac{n^2\pi^2}{l^2} - \frac{\alpha^2}{v^2}}}{C p_m v \text{Cos} \left( \frac{n\pi x}{l} \right)} \quad (45)$$

Substituting the values of  $p_m$  and  $\frac{\partial Z(p_m)}{\partial p_m}$  from (41) and (45) in (2), we get the complete expression for the current on the line.

For constant e.m.f.  $\omega = 0$ , substituting the values of  $p_m$  and  $\frac{\partial Z(p_m)}{\partial p_m}$  in (1), we get after some straightforward simplification:

$$I = \frac{E}{Rl} + E\varepsilon^{-\alpha l} \sqrt{\frac{C}{L}} \sum \frac{\text{Cos} \left( \frac{n\pi x}{l} \right) \text{Sin} \left( \sqrt{\frac{n^2\pi^2 v^2}{l^2} - \alpha^2} l \right)}{l \sqrt{\frac{n^2\pi^2}{l^2} - \frac{\alpha^2}{v^2}}}. \quad (46)$$

Another illustration of the application of the Expansion Theorem is given in my paper "Alternating Current Cable Telegraphy."<sup>2</sup>

<sup>2</sup> JOUR. FRANK. INST., Vol. 195, No. 2, Feb., 1923.



# THE EARLIEST APPARATUS AND PROCEDURES OF PHOTOGRAPHY: CONTRIBUTIONS TO THE CENTENARY OF MODERN PHOTOGRAPHIC METHODS.\*

BY

HENRY LEFFMANN, A.M., M.D.

Lecturer on Research, Philadelphia College of Pharmacy and Science,  
Philadelphia, Pennsylvania; Member of the Institute.

IN 1889 a semi-centennial celebration of the invention of photography was held, especially under the auspices of French photographers, the date relating to the formal announcement by Arago (before the French Academy of Sciences) of Daguerre's method of taking pictures. It is proposed to celebrate in 1923 a *centennial* anniversary, and the question at once arises as to what has become of the sixteen years that should elapse before the centenary of Daguerre's invention will occur. The answer is that while Daguerre perfected a method of taking portraits with the camera after comparatively short exposure, the first actual picture-making by means of light was done by Nicephore Niépce about 1823. It is the centennial of this procedure that France has decided to distinguish.

No such celebration can occur without raising the question of the early history of the procedure and causing disputes as to priority, but the moment the investigator begins to search the records confusion arises. What constitutes discovery or invention? Aristotle and Augustine make allusions that can be interpreted as indicating a theory of evolution, yet they are not quoted as real anticipators of Darwin and Wallace. Scattered through the writings of scientists from the thirteenth century on to the close of the seventeenth, we find more or less incidental allusions to the property of silver salts blackening in contact with organic matter, but the effect was not infrequently ascribed to the action of the air. We should not, however, deal flippantly with such mistakes, for we may note that even as late as the early part of the nineteenth century, when the natural and physical sciences had

---

\* Presented at a joint meeting of the Sections of Physics and Chemistry and Photography and Microscopy, held Thursday, December 14, 1922.



reached a high degree of exactness, the yellow tinge seen in common flames was ascribed to the presence of water. It is now known to be due to sodium salts. The names of Albertus Magnus, Roger Bacon, Fabricius, Glauber and, of course, Leonardo da Vinci, would be mentioned in a summary of these adumbrations, but the data at hand seem to show that the first one to recognize the cause of the blackening of silver salts was Heinrich Schulze, who in 1727 demonstrated the action of light upon a mixture of chalk and silver nitrate, essentially silver carbonate. The mixture was prepared in a glass vessel, a part of which was covered by paper. On exposing to light the precipitate darkened at the unprotected places, but was not affected at the other points. By this means it was shown that the action was not due to either air or heat. It is obvious that, interesting and creditable as Schulze's experiments are, they are not photography in the sense in which the word is understood to-day. An important point is that the results could not be fixed, that is, the effect of the light could not be stopped after the action had gone as far as desired, unless the material was kept in the dark. It is also to be noted that the effects are merely copying; there is no formation of an image of an external object. All modern procedures are the results of invention and discovery along several independent lines. Whether we take instruments of research, such as the telescope and microscope, apparatus for manufacturing, such as the printing press, for transportation, such as the locomotive, or for amusement, such as the motion-picture, we will find them culminations of the labors of many workers. The motion-picture, for instance, depends upon a brilliant light source, a flexible film, a high-speed emulsion, excellent lenses, active developing and fixing materials and mechanical appliances. So in modern photography, many have had a share in the progress, and it is difficult and even invidious to give the honors to a few. The bridge built some years ago over the Susquehanna, at Havre de Grace, bore a tablet stating that it was the work of "a thousand men for four years," and similarly our modern photographic procedures may be described as the work of hundreds of investigators for several centuries.

Light has wide range of action; few substances, if any, are wholly immune, but in most cases the changes are but slowly produced and very slight. A few substances show great suscepti-



bility, the silver salts being, so far as ascertained, preëminent in this respect. In modern photography, therefore, silver dominates, and it is especially the chloride, bromide and iodide that are employed, these being conveniently included under the title "silver halides." Light produces a prompt visible effect upon silver chloride, which is darkened, but the other halides show no visible effect except upon prolonged exposure. Notwithstanding this lack of change in appearance, it is easily shown that even exceedingly brief exposures of silver bromide or iodide produce a marked change, which can be demonstrated by the precipitation of silver and some other metals—upon the parts that have been touched by the light. It has been a question whether the light acts by producing chemical decomposition or merely changes the substances physically. Considerable investigation has been carried out to determine this point. For convenience, the area of the halide affected invisibly by the light is called the "latent image." Two views as to the chemistry of the latent image are now in vogue. One is that sub-halides are formed by action of the light; the other is that a complete decomposition of a limited number of molecules takes place and that the silver thus set free is in colloidal condition. Under either theory it seems reasonable to assume that a difference of electric potential will be produced, respectively, in the parts touched and not touched by the light, and as the subsequent production of the image by development is due to the precipitation of metallic silver, a selective attraction will be the result. It is, however, not within the scope of this paper to discuss the problem to any extent. Some salts of mercury and copper are distinctly sensitive to light, although not nearly so much as the silver halides. Mercurous iodide, which is a bright yellow powder, undergoes, with moderate rapidity when exposed to a strong light, a conversion into a black powder. Presumably, this effect is due to the separation of metallic mercury in a state of fine division, in which its familiar lustre is lost. This property of mercurous iodide was studied in 1836 by Artus (*J. prak. Chem.*, 1836, viii, 63). In many cases the effect of light can be increased, in extent or rapidity, by the addition of a third substance, which may be unaffected, thus acting the part of catalyst, or may take definite part by combining with the liberated element, thus preventing a saturation or equilibrium, which would interfere with further action. It is now well known that many rays of



light are invisible to the human eye, but have active chemical and physical effects. Rays that are beyond the violet, which is the upper limit of the visible spectrum, have a powerful effect on silver salts.

The sensibility of silver salts to light would have had but a narrow field of application if it was not possible to project the image of any object in correct form upon a sensitized surface. That is, some optical arrangement must be employed. Schulze secured a contrast between light and darkness, but he constructed the picture—at least, we may for sake of argument call it a picture—and devised no method by which a natural object or design could be repeated on his mixture of chalk and silver nitrate. Niépce also copied designs by superposition. Other workers, especially Davy and Wedgwood in England, made experiments along these lines. They employed different materials coated with silver nitrate which blackened under the light, but such changes are too slow, even if apparatus was available, and moreover, as noted above, the prints could be preserved only in the dark.

The invention of the camera is a most important phase of the development of photography. The word goes back to a Greek word, "kamara," meaning anything with a vaulted or arched cover. It came to mean "room," especially a vaulted room, and after suffering several etymologic evolutions it has become the regular term for room in several European languages. It is the familiar instrument in all departments of photography, and probably as much mechanical ingenuity has been applied to it as to any other machine. The evolution of it from the clumsy, heavy and expensive form of Daguerre's day to the "push the button and we do the rest" of the modern amateur, would require pages to detail. Coincident with the evolution of the form of the camera itself, has gone the improvement in the lens, extending its field, improving its definition and increasing its speed.

The camera is an invention of several centuries ago. It is usually ascribed to an Italian, John Baptist della Porta, but some doubt exists as to how far he actually originated it. He developed the apparatus a great deal, and described it in a work in several volumes, which appeared during the years 1558-1589. This work was translated into several languages, an English edition appeared about a century after the original text. The title "camera obscura" refers to the fact that the room was dark



except so far as it was illuminated by the image transmitted through a lens. The modern camera in all its forms can be traced back to the apparatus della Porta described, but the formation of images is not dependent on a lens. A minute opening is capable of forming a complete picture, indeed the perspective is better than that obtained with almost any lens. To obtain a perfect image in this way, the opening should be so small as to

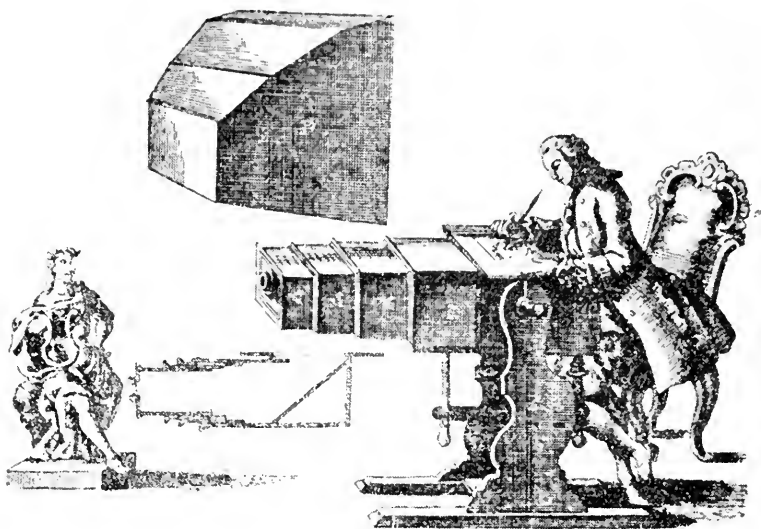


Kircher's camera (1671).

admit only single rays of light from all points, a condition that is not capable of being realized in practise. The opening, therefore, gives a slightly confused image, but this is no objection in landscape and architectural photography. In practise an opening about large enough to pass a small needle is made through a metal plate, quite thin at the point of perforation. Care must be taken that no bur is present; the metal must be perfectly flush on each side. Such an arrangement is usually termed a "pin-hole." Pinhole pictures have been made by many workers, and according to Eder (*Geschichte der Photographie*) a precise description of such a method of projecting images of external objects was first given by Leonardo da Vinci, who stated that when a building or a landscape is brilliantly illuminated by the



sun, an inverted image can be obtained by means of a small perforation in the wall of an opposite building. He states that the opening should be very small and neat, and further that the formation of the image is akin to the formation of the image on the retina, the pupil acting as the opening. It is a remarkable anticipation of the pinhole method, but it must not be overlooked that the eye acts by means of its lens system, and that the pupil opening is too great to form a clear image on the retina. These



Early camera lucida.

discoveries of Leonardo were doomed, like many that he made, to be practically fruitless, being locked up in his writings, difficult to read and long deferred in publication. It is, therefore, not possible to say how far some of the later workers in this field owe their inventions and discoveries to accidental knowledge of Leonardo's work or made independent developments.

As noted above, pinhole pictures give better perspective than lenses, and are especially suitable for architectural subjects and some classes of landscapes. The exposure is long, being ordinarily sixty times that required with a rapid lens, so that if a given combination will give a good picture with one second exposure, a pinhole substituted for the lens will entail a one-minute period. Moving objects, unless quite slow, are not taken, so that



a pinhole camera may be employed on the side of a road over which automobiles are passing without appreciable record of these. The picture also has a softness which is not usual with those made with lenses, although modern expedients are now available by which extreme softness may be obtained by the standard cameras. These extreme degrees may be imitated to a limited extent by using a pinhole of larger diameter, but no particular advantage is gained. The minute opening is, of course, unsuited for photomicrography, in which microscopic sharpness is required.

Investigation has been carried on with great earnestness since the days of Daguerre, for his procedure made photography of wide practical value, and many methods of procedure have been devised. The daguerreotype, though highly artistic, has the disadvantage that each picture required a separate sitting, and the same was true of the ambrotype, which was made by producing a thin negative on glass and then mounting this with a black backing. The invention of the paper positive gave at once the most desired feature to picture-making, namely, the ability to produce any number of positives from one exposure. Subsequently the wet collodion process which was an early method of making glass negatives was applied to the ferrotype or "tin-type," as it was familiarly called. In this a sensitized collodion film was spread on lacquered sheet iron, and when developed and fixed gave a pleasing portrait. In this, as in the daguerreotype, each picture required a separate sitting, but this difficulty was overcome during the vogue of the method, by multiple lenses, such as four in a group, and a sliding arrangement by which four exposures could be made on one sheet, thus obtaining sixteen pictures. It is not necessary to follow the details of commercial photographic development as the principal features are well and generally known.

The introduction of desensitizers is an important and very recent feature of photography. As in all other cases, the existing methods were in a way anticipated, for many years ago it was shown that the ferrous oxalate developer diminishes materially the sensitiveness of the ordinary dry-plate emulsion, so that the development may be carried out in a brighter light than usual, but this method did not come into practical use. A couple of years ago, Lüppo-Cramer, a Munich chemist, discovered, as a result of trials of many substances, that a dyestuff known as "pheno-



safranin," had power to diminish the sensitiveness of the common emulsions, without appreciably diminishing the latent image, that is, the undeveloped impression on the plate. A solution of 1 gram to 1000 c.c. (15 grains to the 1 quart) will serve for many plates. After exposure, the plate is immersed for a couple of minutes in the solution (in darkness, of course), briefly washed, and immersed in the developer. The immersion in the dye so far abates the sensitiveness, that plates that require green light can be safely developed by the ordinary red light, and those requiring red light can be developed in yellow. The plate is



Stereoscopic drawings (supposed fourteenth century).

stained, but this can be removed by washing or by certain chemicals. In most cases the stain does interfere seriously with the use of the negative. The solution stains the hands, and it is well, therefore, to use rubber finger cots. After the plate is fixed and washed there is no danger of staining the hands. Lumière and Seyewitz made many experiments with a view of discovering substitutes for phenosafranin, but found little of importance. A yellow dye, "aurantia," was found to have marked desensitizing power, but has no special advantage. Lüppo-Cramer published the composition of the desensitizer, with the result that it was introduced into commerce in other countries under trade names, and the inventor deprived of both honor and profit of his discovery. He has since introduced two new dyes, the composition of which he has not made known, designating them simply as "pinakryptol" and "pinakryptol green," respectively.



A remarkable modification of photographic procedure is developing after fixing. Several methods have been long known, but none has special practical value. It is of considerable theoretical interest inasmuch as it has a bearing on the nature of the latent image, for by means of a weak fixing bath, all the sensitive emulsion can be removed, as far as can be judged by the eye, yet after washing thoroughly in order to get rid of the soluble salts, the image can be brought out fully by means of



Pinhole photograph.

several forms of developer, among the simplest of which is a solution containing metol, mercuric bromide and sodium sulphite. The following experiment shows the remarkable persistence of the image. A plate was exposed for several weeks in perfect darkness close to, but not in actual contact with, a plate of common amalgamated battery zinc. It was then immersed in a weak fixing bath until all trace of emulsion was removed, washed and immersed in the above-mentioned developer. The development was carried in the light. A strong image was obtained. The plate was mounted as a lantern slide, and afterward put away for a couple of years with other slides. The image gradually disappeared, and finally only a few small spots were left. The plate was again immersed in the special developer, and



in a few minutes the image appeared in good strength. It seems that the latent image may reside on gelatin as much as in the silver halide.

Finally, as an interesting instance of how difficult it is to fix definitely the time and place of scientific discovery, and to assign honors, therefore, an illustration is appended taken from the *Bulletin of the French Society of Photography* (3rd ser., 1922, ix, 206). It shows twin pictures drawn by an artist so that, when viewed in the stereoscope, a good impression of solidity is produced. The fact that the impression of solidity is given by the joint action of both eyes was known to Euclid, three centuries before the beginning of the common era and also to Galen five centuries later, but this knowledge, as was the case with much other information, appears to have been practically lost during the dark ages. Prominent workers in the early period of the revival of learning, *e.g.*, da Vinci and Porta, revived this knowledge, but it was left to Wheatstone in 1838 to devise a special instrument for producing effects of solidity from two pictures representing the image by each eye, respectively. The effect was produced by mirrors. The instrument was called a "stereoscope." Much later, Brewster devised one in which lenses are used, which became the regular form. The illustration taken from the French journal shows a stereoscopic combination that is stated to have been drawn in the fourteenth century, by an artist named Jacopo Chimenti, and is now in the Wicar Museum at Lisle. The drawings are in different ink, one red, the other black. It does not appear that there is any record of an apparatus constructed for viewing the pictures, but the matter is of great interest in the history of stereoscopy.

Research Laboratory,

Wagner Free Institute of Science,  
Philadelphia, Pa.

---

**Optical Constants of Sodium-potassium Alloys.** RAYMOND MORGAN. (*Phys. Rev.*, Sept., 1922.)—Drude's method of obtaining the optical constants of metals was used for a series of these alloys. The index of refraction for potassium is .060 and for sodium .047. For all alloys of these two metals the index is greater than that of either of the two constituent metals. The maximum value is .137 and is for an alloy having 66 per cent. of potassium by weight. In the case of an alloy containing 82.7 per cent. of sodium, a solid, a diminution of the refractive index with rising temperature was observed.

G. F. S.



# STUDIES IN PHOTOGRAPHIC SENSITIVITY.\*

## II

### THE ACTION OF HYDROGEN PEROXIDE ON PHOTOGRAPHIC GELATINO-SILVER HALIDE EMULSIONS.

BY

S. E. SHEPPARD and E. P. WIGHTMAN.

Research Laboratory of the Eastman Kodak Company.

#### INTRODUCTION.

It has been known for a long time that both the vapor and the solution of hydrogen peroxide have an action on the photographic plate somewhat similar to that of light.

W. J. Russell,<sup>1</sup> in 1899, was the first to give any quantitative data concerning this action. He stated that "if the liquid contains only one part of peroxide in 1,000,000 of water and the plate be exposed to its action, *i.e.*, of the vapor, for 18 hours a faint picture is produced. Bearing in mind the small amount of evaporation which takes place under these conditions and consequently the minute amount of hydrogen peroxide which comes in contact with the plate, it clearly shows the exceeding delicacy of the reaction." Even when he interposed thin sheets of gelatin, celluloid, etc., between the  $\text{H}_2\text{O}_2$  and the plate, action took place.

The work of Russell has since been substantiated, as well as elaborated, by others who have compared more in detail the action of  $\text{H}_2\text{O}_2$  on the photographic plate with that of light. Among the more important investigations may be mentioned that of Precht and Otsuki.<sup>2</sup> They showed that the action increases with the concentration of  $\text{H}_2\text{O}_2$  up to a maximum and then decreases again. It depends upon the amount of  $\text{H}_2\text{O}_2$  vaporized in unit time, and is, following the evaporation of a mixture of  $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$ , greater for 3 per cent. than for 30 per cent.  $\text{H}_2\text{O}_2$ .

They found further that for equal concentrations the action increases with time of exposure up to a maximum beyond which

---

\* Communicated by Dr. C. E. K. Mees, Director of Laboratory and Associate Editor of this JOURNAL. Published as Communication No. 158 from the Research Laboratory of the Eastman Kodak Company.

<sup>1</sup> *Phot. Jour.*, 23, 198, 234 (1899).

<sup>2</sup> *Ann. Physik.*, 4, 16, 890 (1905).



a reversal similar to solarization sets in. All their measurements were made by exposure to the vapor at 1 cm. from the surface of the liquid.

Dombrowsky<sup>3</sup> also carried out a very extensive investigation on the action of the vapor of  $\text{H}_2\text{O}_2$ . He believed that  $\text{H}_2\text{O}_2$  acts in steps: (1) A relatively quick adsorption, (2) a relatively slow chemical reaction with the silver halide-gelatin. The blackening on development is the result of both.

He found that the reciprocity law

$$It = \text{const.}$$

does not hold for the action of  $\text{H}_2\text{O}_2$  if  $I$  represents the molar concentration of  $\text{H}_2\text{O}_2$ , and  $t$  the time of exposure to the vapor at a given distance from the liquid surface.

Likewise, the Hurter and Driffield expression<sup>4</sup>

$$D = \gamma \text{Log} \frac{It}{i}$$

was found not to hold for the action of  $\text{H}_2\text{O}_2$  but an equation of the form

$$D = at - b,$$

*i.e.*, linear, does hold approximately. The constants  $a$  and  $b$  depended upon the experimental conditions.

Finally, he observed an effect with long exposures similar to solarization with light.

This paper includes a very good bibliography of the action of metals and of  $\text{H}_2\text{O}_2$  on the photographic plate.

O. and A. Dony-Henault,<sup>5</sup> in 1909, gave some interesting figures concerning the vaporization of  $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$  mixtures and the action of  $\text{H}_2\text{O}_2$ . From their experiments they concluded that the action of the  $\text{H}_2\text{O}_2$  is not due to a radioactive phenomenon, but to chemical action of the  $\text{H}_2\text{O}_2$  vapor. The effect followed the partial pressures of  $\text{H}_2\text{O}_2$  vapor in mixtures of  $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$  which were greater in the smaller than in the higher concentrated solutions. A 12 per cent. solution in 24 hours gave off 0.88 mg.  $\text{H}_2\text{O}_2$ , whereas a 30 per cent. solution in the same time gave 0.56 mg. This agrees with the conclusion of Dombrowsky which they do not mention.

The most important value which they give is, that on 1 cm.<sup>2</sup>

<sup>3</sup> Constantin Dombrowsky, *Inaug. Dissert.*, Leipzig, 1908, p. 68.

<sup>4</sup> *J. Soc. Chem. Ind.*, 9, 455 (1890).

<sup>5</sup> O. and A. Dony-Henault, *Bull. Soc. Belg. Chim.*, 22, 224 (1909).



of the plate  $1.2 \times 10^{-8}$  gm.  $\text{H}_2\text{O}_2$  will produce a photographic latent image. The time of action of this quantity is not stated.

Until recently all measurements on the action of  $\text{H}_2\text{O}_2$  had been made on the ordinary photographic plate. Svedberg<sup>6</sup> was the first to make any measurements of this action on the ultimate grains of the photographic emulsion (in one-grain-layer plates). The data which he gave were meagre and of diminished value because of the interference of "fog," that is, of the large percentage of grains already developable prior to the  $\text{H}_2\text{O}_2$  or light treatment.

The object of the present investigation was to compare the action of hydrogen peroxide on the photographic emulsion with that of light. There are two aspects to this, which may be termed macroscopic and microscopic. In the first, we may measure photographic density  $D$ , which is proportional to mass of silver, determined as a function of conditions of exposure to peroxide, and ascertain if laws similar to photographic light action obtain. It has been proposed<sup>7</sup> to term the action of chemicals such as peroxide "photechic."<sup>8</sup> In the second, we have to determine, using "one-grain layers,"<sup>9</sup> the relation between the number and size of grains made developable by peroxide (photechically) as also, the distribution of development nuclei in the grains, as recently investigated by Svedberg<sup>10</sup> for the action of light.

In order that inference from the second—the microscopic aspect—as to the nature of sensitiveness, developability, the latent image, etc.,<sup>11</sup> should be applicable to the photographic process, it requires to be shown that both macroscopically and microscopically the phenomena are quantitatively comparable. The present investigation is concerned only with the macroscopic side, and we shall show that the photechic action of hydrogen peroxide is entirely similar in effect to the photographic action of light.

---

<sup>6</sup> The. Svedberg, *Zeit. wiss. Phot.*, 20, 36 (1920).

<sup>7</sup> H. Blaas and B. Czermak, *Eder's Jahrb. f. Phot.*, 1904, p. 274. Originally with reference to substances photographically active after illumination.

<sup>8</sup> From Gk. *phos* = light, and *ekhein* = to hold.

<sup>9</sup> The. Svedberg, *loc. cit.*; E. P. Wightman, A. P. H. Trivelli, S. E. Sheppard, J. FRANK. INST., 194, 485 (1922).

<sup>10</sup> The. Svedberg, *Phot. J.*, 62, 310 (1922) (Third Hurter and Driffeld Memorial Lecture).

<sup>11</sup> Cf. Svedberg, *loc. cit.* We have discussed the whole problem fully in a paper in the JOURNAL OF THE FRANKLIN INSTITUTE, 194, 485 (1922).



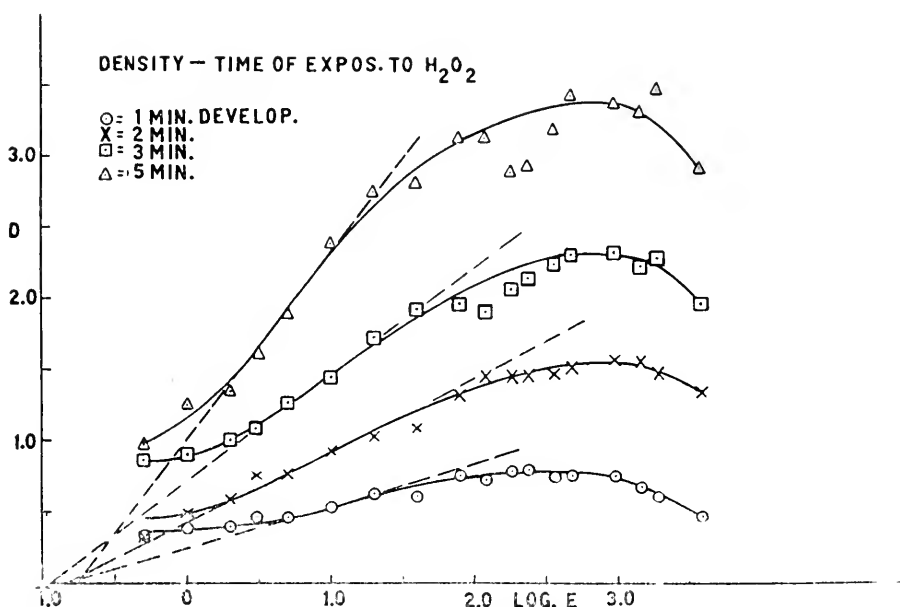
## EXPERIMENTAL.

The factors of the peroxide effect which demand attention are:

1. The intensity factor, as function of concentration.
2. The time factor on exposure at constant concentration.
3. The effect of acidity or alkalinity on the peroxide effect.
4. The course of development of peroxide treated plates.
5. The behavior of different emulsions.

The actual experimental method was as follows: A number of strips about  $2 \times 10$  cm. were cut from plates or films of the

FIG. 1.



emulsion studied. These were dipped, in pairs, back to back, in separate beakers containing about 30 c.c. each of the hydrogen peroxide solution, at a constant temperature of  $20^\circ C$ . After this exposure the pairs of strips were washed for one-half hour in separate beakers in rapidly running water. They were then developed in 1:1 pyro-soda developer,<sup>12</sup> stopped in 1 per cent. acetic acid solution, rinsed, fixed, washed and dried under

<sup>12</sup> A. $Na_2SO_3$ (anhyd.)	64.0 grams
$NaHSO_3$	17.5 grams
Pyro	20.0 grams
$H_2O$ to	1 litre
B. $Na_2CO_3$ (anhyd.)	75 grams
KBr	1 gram
$H_2O$ to	1 litre



standard conditions. Densities were measured with a Martens photometer.

*A. Time of Exposure, and Time of Development.*

The curves (see Fig. 1 plotted from data in Table I) relating density  $D$  to the logarithms of the times of exposure, for different times of development are quite similar to the well-known photographic characteristic or  $H.$  and  $D.$  curves. They have an "underexposed portion" or "toe," in which the density varies linearly with the exposure time; an approximately "straight line" portion, where  $D \propto \log t$ , although this is relatively short for the peroxide effect; an "overexposed" portion; a maximum; and a "reversal" phase. At the same time, the straight line portions, for different times of development, or the family of tangents to the inflexion points of the curves, tend to approach a common convergence point on the  $\log t$  axis, comparable to the inertia of photographic sensitometry.

TABLE I.

*Density-Time of Exposure.*

$\text{H}_2\text{O}_2 = 0.300 \text{ M}$ ;  $\text{pH} = 3.3$ ;  $T = 20^\circ \text{ C}$ .

Time of Development = 1, 2, 3 and 5 Min. in 1:1 Pyro-soda at  $20^\circ$

Rinsed in 1 per cent. Acetic Acid for 3 sec.

Fixed in Acid Hypo for 15 Min.

Plate No.	Time in Sec.	$\log t$	$D_1$	$D_2$	$D_3$	$D_5$
1	0.5	1.70	0.33	0.32	0.86	0.98
2	1	0	0.38	0.49	0.91	1.25
3	2	0.30	0.39	0.58	1.01	1.35
4	3	0.48	0.46	0.75	1.08	1.61
5	5	0.70	0.46	0.76	1.27	1.89
6	10	1.00	0.53	0.92	1.43	2.39
7	20	1.30	0.62	1.02	1.72	2.75
8	40	1.60	0.60	1.08	1.93	2.81
9	80	1.90	0.75	1.31	1.96	3.13
10	120	2.08	0.72	1.45	1.91	3.13
11	180	2.26	0.78	1.45	2.06	2.89
12	240	2.38	0.79	1.45	2.14	2.94
13	360	2.56	0.74	1.46	2.24	3.20
14	480	2.68	0.75	1.51	2.31	3.43
15	960	2.98	0.75	1.56	2.33	3.39
16	1440	3.16	0.67	1.55	2.23	3.32
17	1920	3.28	0.60	1.47	2.28	3.47
18	3840	3.58	0.46	1.34	1.96	2.91



B. *Effect of Increasing Concentration of Hydrogen Peroxide, the Time of Exposure Being Kept Constant.*

In these experiments—concentrations higher than 1 gm. mol. per litre were not attained, and the experiments will be pushed further.

FIG. 2.

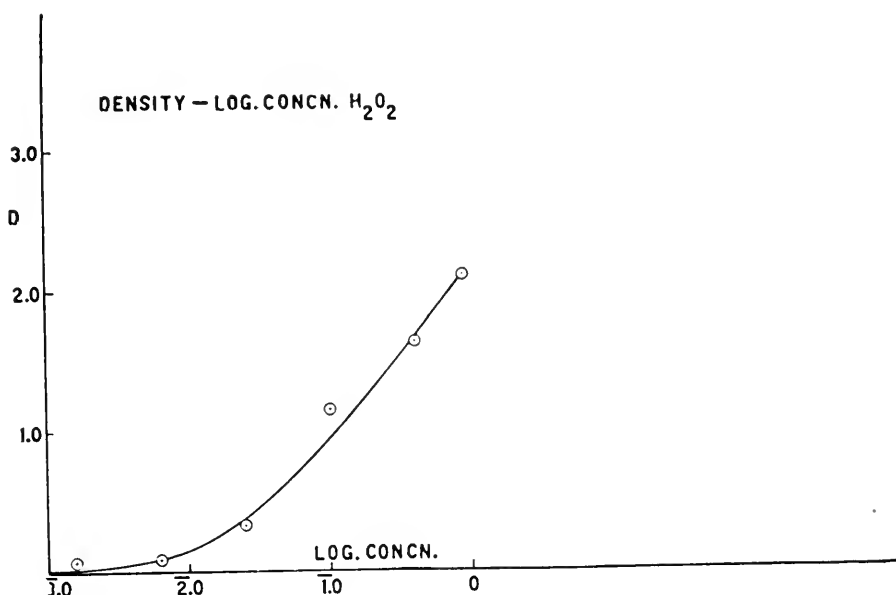


TABLE II.

*Density-Concentration of  $H_2O_2$ .*

Time of Exposure, 1 Min.

Time of Development, 3 Min. in 1:1 Pyro-soda at 20°

Rinsed in Acetic Acid and Fixed as in Table I.

Soln. No.	Conc. in Mol. / L.	Log C	pH	Dm	Molecules $H_2O_2$ per c.c.	Molecules $H_2O_2$ per 1 cm. <sup>2</sup> x 0.01 mm.
1	0.882	1.95	3.4	1.98	$5.34 \times 10^{20}$	$5.34 \times 10^{17}$
2	0.400	1.60	3.7	1.63	$2.42 \times 10^{20}$	$2.42 \times 10^{17}$
3	0.100	1.00	4.2	1.15	$6.06 \times 10^{19}$	$6.06 \times 10^{16}$
4	0.025	2.40	5.6	0.33	$1.52 \times 10^{19}$	$1.52 \times 10^{16}$
5	0.0063	3.80	6.4	0.09	$3.82 \times 10^{18}$	$3.82 \times 10^{15}$
6	0.0016	3.20	7.0	0.07	$9.7 \times 10^{17}$	$9.7 \times 10^{14}$
7	0.0004	4.60	7.0	0.07	$2.4 \times 10^{17}$	$2.4 \times 10^{14}$
8	0.0001	4.00	7.0	0.06	$6.1 \times 10^{16}$	$6.1 \times 10^{12}$
9	0.00002	5.30	7.0	0.06	$3.0 \times 10^{16}$	$3.0 \times 10^{13}$

From results so far obtained, it appears that the effect of increasing concentration is similar to that of increasing light intensity. (See Fig. 2 plotted from data in Table II.)



C. *Effect of Hydrogen Ion Concentration.*—The reducing power of hydrogen peroxide is increased in alkaline, diminished in acid solution.<sup>13</sup> It is, therefore, of interest to note that its action on the photographic emulsion is reduced by increasing the alkalinity. It will be remembered that in these experiments the plates are dipped in the solution. The relation of the density to the Sørensen value of the solution is shown in Table III, and it is seen that over a range of *pH* values from about 4 to 7, *i.e.*, from fairly acid to the neutral point, there is very little change in the density.

TABLE III.

*Density-pH.*0.175 M H<sub>2</sub>O<sub>2</sub> at 20°

Developed 3 Min. in 1:1 Pyro at 20°

1 per cent. Acid Short Stop for 3 Sec. Fixed in Acid Hypo.

Soln. No.	<i>pH</i>	Indicator.	<i>D</i> <sub>1</sub>	<i>D</i> <sub>2</sub>	<i>D</i> <sub>3</sub>	<i>D</i> <sub>4</sub>	<i>D</i> <sub>m</sub>
1	2.2	Thym. Blue	1.52	1.50	1.50	1.52	1.51
2	3.6	Br. Phen. Blue	1.52	1.58	1.39	1.43	1.48
3	3.8	Br. Phen. Blue	1.17	1.37	1.23	1.16	1.23
4	4.0	Br. Phen. Blue	1.16	1.21	1.27	1.21	1.21
5	7.2	Br. Cres. Blue	1.23	1.32	1.31	1.10	1.24
6	9.2	Thym. Blue	1.02	1.16	1.01	0.92	1.03

While not very sensitive, these results indicate that whatever chemical action of the peroxide is involved, it can hardly be an incipient reduction of the silver salt.

D. *Growth of Density and Gamma, with Time of Development.*

TABLE IV.

*Density-Time of Development.*H<sub>2</sub>O<sub>2</sub> = 0.295 M; *pH* = 3.3 = Temp. = 20°

Developed in 1:1 Pyro at 20°

Soln. No.	Time of Development.	<i>D</i> <sub>m</sub>	$\gamma$
1	0.5 min.	0.03	
2	1.0	0.21	0.29
3	1.5	0.51	
4	2.0	0.72	0.52
5	2.5	1.14	
6	3.0	1.31	0.77
7	4.0	1.57	
8	5.0	1.65	1.32
9	10.0	2.47	

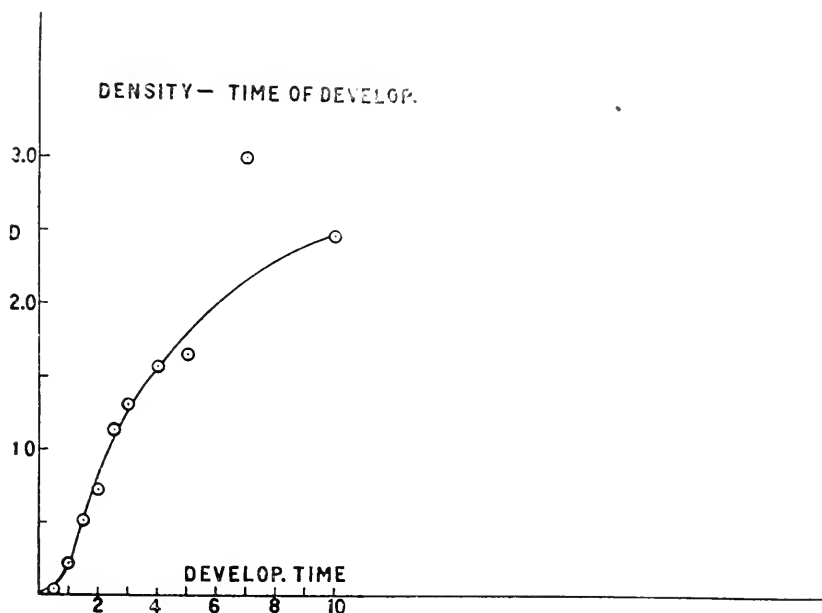
<sup>13</sup> Cf. Sheppard and Mees, "Investigations," p. 148.



(Of minor importance for the question at issue, but confirming the parallelism with photographic action, is the growth of density and contrast with time of development (see Figs. 3 and 4). It will be seen that the density increases rapidly at first, then gradually tends to a limit, as found for photographic exposures. Terming  $\gamma$  the slope of the straight line portion<sup>14</sup> of the "characteristic,"  $D = \gamma \log \frac{t}{t_0}$  this will follow a similar law in respect to time of development.

*Discussion of Results.*—The similarity of the action of hydrogen peroxide to that of light, as disclosed by these results, is very

FIG. 3.



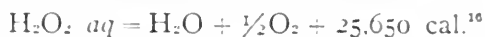
striking. Before drawing definite conclusions, however, we propose to obtain further data, particularly to observe whether the photographic light "speeds" of the emulsion parallel the peroxide "speeds" or sensitivities, and further to examine the microscopic behavior in the manner being carried out for the action of light. Meanwhile, we wish to propose the following tentative hypothesis. It has been shown to be very unlikely that the peroxide is acting as a reducing agent on silver halide. The suggestion of Lüppo-Cramer<sup>15</sup> that its action is due to an oxidative attack on the gelatin protecting the silver halide grains does

<sup>14</sup> Or the tangent at the point of inflexion.

<sup>15</sup> *Phot. Korresp.*, 1902, p. 563.

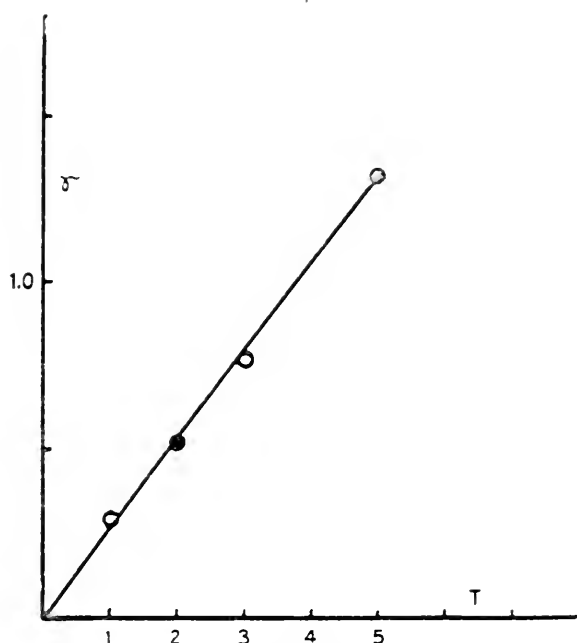


not seem probable, in view of the great sensitiveness of the reaction. We, therefore, suggest that since hydrogen peroxide is endothermic in its formation from water



and is continually decomposing, especially in presence of catalysts, that the energy is evolved primarily as a chemi-luminescence, of short wave-length affecting the silver halide. Further, if it be supposed that this decomposition is catalyzed by the photo-sensitizing nuclei of the grains, the presence of which we have discussed

FIG. 4.



elsewhere,<sup>17</sup> a still closer parallelism to the photographic behavior of the *same emulsion* should obtain. If this is found, it will strengthen the view that the sensitiveness nuclei (ripening germs) in the silver halide grains, consist of colloid silver.

In connection with the quantum theory of photographic exposure<sup>18</sup> it is of interest to find the ratio of silver halide grains in the emulsion to the number of molecules of hydrogen peroxide in the vicinity. In the plates used the number of grains was of the order  $10^9$  per sq. cm., but these lie in some 10 to 30 layers, none of which covers the whole surface. Taking the concentra-

<sup>16</sup> Lewis and Randall, *J. Am. Chem. Soc.*, 36, 1964 (1914).

<sup>17</sup> S. E. Sheppard, *Phot. J.*, 62, 88 (1922); E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard, *J. FRANK. INST.*, 194, 485 (1922).

<sup>18</sup> L. Silberstein, *Phil. Mag.*, 44, 257 (1922).



tions of peroxide in Table V, and assuming a layer of thickness .01 mm., as the minimum effective thickness, the number of molecules in this layer can be obtained.

TABLE V.

Concn. $\text{H}_2\text{O}_2$ in mol. / l	Moles of $\text{H}_2\text{O}_2$ per 1 sq. cm. x .01 mm. of plate
.882	$5.34 \times 10^{17}$
.4	$2.42 \times 10^{17}$
.1	$6.06 \times 10^{16}$
.025	$1.52 \times 10^{16}$
.0063	$3.82 \times 10^{15}$
.0016	$9.7 \times 10^{14}$ or approx. $= 10^{15}$

From this it appears that in a layer of peroxide  $1 \text{ cm.}^2 \times .01$  mm. depth the number of molecules at the lowest concentration producing a developable image on 3 minutes development is of the order  $10^{15}$ . From kinetic considerations of diffusion, the available molecules would be actually higher. On the basis of Dr. L. Silberstein's theory of exposure these molecules would be equivalent to light darts or quanta, the effective "exposure" depending upon the chance that a molecule of peroxide collide with a silver halide grain, and form a developable nucleus. Although the data for one-grain layers are necessary before drawing any rigorous conclusions, it is evident *that the density of peroxide molecules at which only a few of the silver halide grains are affected is very high, viz.,  $10^{15}$  molecules:  $10^9$  grains.* Consequently, it must either be assumed that the grains differ amongst themselves inherently as regards sensitivity, or, to conserve the quantum parallel, that the proportion of "active" peroxide molecules is very small.

## SUMMARY.

1. The sensitometric characteristics of photographic plates exposed to hydrogen peroxide and developed are strikingly similar, both for time of exposures, time of development, and intensity (*i.e.*, concentration). Characteristic curves similar to *H.* and *D.* curves were obtained, including a period of "reversal."

2. A tentative theory of the action of hydrogen peroxide is suggested. It is supposed that the decomposition of peroxide is chemi-luminescent, short wave-length radiation being afforded at the surface of the silver halide grain, and particularly at



photosensitive nuclei. It is hoped that the reaction may be used to check the hypothesis that these nuclei consist of colloid silver.

The authors desire to express their thanks to Mr. R. F. Quirk and Mr. E. Huberth for painstaking assistance in the experimental work, and to Miss Anber J. Benedict for making the  $pH$  measurements.

*Errata in Part I, this JOURNAL, 194 (1922).*

1. p. 502, equation (b) should read  $\frac{dx}{dt} = k' I.S (a-x)$ , etc., instead of  $\frac{dx}{dt} k' I.S (a-x)$ .

2. p. 503, under "Equation Type B" first column, omit Roman numeral II; fourth column, lower  $D = D_m (1 - e^{-k'E})$  to second row.

3. p. 518, last equation, instead of  $\left\{ 1 + (n + \mu) S_1 e^{-(\mu + n) S_1} - \text{etc.} \right\}$  read  $\left\{ \left[ 1 + (n + \mu) S_1 \right] e^{-(\mu + n) S_1} - \text{etc.} \right\}$

4. p. 520, first line last word should read "desensitizing" instead of "densitizing."

5. p. 520, Summary, paragraph 2, last line, read "inertia-variation" instead of "intensity-variation."

ROCHESTER, N. Y.,

Oct. 8, 1922.

**Test for Acrolein.**—WILMER C. POWICK, of the U. S. Bureau of Animal Industry (*Ind. Eng. Chem.*, 1923, xv, 66), has devised the following test for acrolein. Several drops of the dilute solution of acrolein are mixed with one drop of approximately 3 per cent. hydrogen peroxide. Then five c.c. of concentrated hydrochloric acid are added; and the resulting solution is shaken with five c.c. of a 1 per cent. solution of phloroglucinol in ether. A deep red color immediately appears in the aqueous layer. The pigment separates as a purple precipitate if an excess of acrolein be present. The aqueous solution of the pigment is characterized by a well-defined, fairly narrow absorption band in the yellow-green region. The absorption spectrum is identical with that of the pigment formed in the Kreis test for rancidity of fats and oils.

J. S. H.

**New Vitamin.**—HERBERT M. EVANS and K. SCOTT BISHOP (*Science*, 1922, lvi, 650-651) have discovered a hitherto unrecognized dietary factor which is essential for the reproduction of animals. It is tentatively designated x, and is not identical with any of the vitamins hitherto known. It occurs abundantly in fresh green leaves of lettuce and is apparently present in dried alfalfa leaves.

J. S. H.



**Effect of Water on Zinc Chloride.**—This substance, one of the most efficient preservatives for wood, suffers much loss if the wood is exposed to water. Curiously, water causes a decomposition of the salt, removing material amounts of chlorine. Samples of preserved wood analyzed after service were found to contain zinc equivalent to 0.4 and chlorine only sufficient for 0.08. In examining treated wood, therefore, it is important to determine the chlorine as well as the zinc, since it is the chloride and not the zinc alone which gives protection. Even then some of the chlorine must be considered liable to be in the form of an insoluble compound. (Tech. Notes, Forest Products Lab.)  
H. L.

**Use of Blue-stained Lumber.**—This stain is due to a fungus in the sapwood and does not materially affect the strength of the wood. No method of killing the fungus has been found except kiln-drying. Re-surfacing will not avail when the fungus has made substantial penetration. Many uses, however, can be made of lumber so stained. (Tech. Notes, Forest Products Lab.)  
H. L.

**On the Distribution of Radioactive Bodies in Solutions.** H. LACHS and MATHILDE WERTENSTEIN. (*Physikal. Z.*, Aug. 15, 1922.)—A neutral solution of polonium was put in a burette. After a time samples were taken from the upper and from the lower parts and their radioactivity was determined. Except in the single case of the solution having been let alone one minute only there was a much higher radioactivity in the lower sample. No such difference was found when the solution was acid, but in an alkaline solution the difference between the layers was even more marked than in the neutral solution. More elaborate experiments in which samples were drawn from five levels of the liquid confirmed the previous conclusion that there is a progressive increase in radioactivity from the top of the liquid downward. Similar results were obtained with solutions containing radium alone or RaD and RaE together.

Somewhat corresponding properties of the radioactive solutions had been noted by other experimenters in respect to dialysis and Paneth had concluded that polonium in neutral solutions exists in the colloidal state. The present authors are able to fix approximately the size of the colloidal particles, but they hold that only a part of such particles can be made up of radioactive matter. It has been shown that carefully distilled water contains in a cubic centimetre some tens of thousands of foreign particles visible under the ultra-microscope. Under the influence of gravity these arrange themselves in the liquid so that they are most frequent in the lowest layers. To these the radioactive particles attach themselves. The differences in distribution are characteristic not of the radium or other radioactive substances in solution, but of water containing colloidal particles.

G. F. S.



# A SURVEY OF EXISTING CRYSTAL STRUCTURE DATA.\* †

BY

RALPH W. G. WYCKOFF, Ph.D.

Physical Chemist, Geophysical Laboratory, Carnegie Institution of Washington.

## SULFIDES, SELENIDES AND TELLURIDES.

**MONOSULFIDES, ETC.**—Of the few crystals for which structures have been determined only zinc blende,  $\text{ZnS}$ , and alabandite,  $\text{MnS}$ , have received satisfactory treatment. The others to which assignments of structure have been made are wurtzite ( $\text{ZnS}$ ), greenockite ( $\text{CdS}$ ), galena ( $\text{PbS}$ ) and strontium selenide.

*Alabandite*,  $\text{MnS}$ .—From spectrographic and powder photographic data and the results of the theory of space-groups it has been shown<sup>84</sup> that alabandite either has precisely the "sodium chloride arrangement" (Fig. 6) or one very close to this grouping. The possibility of such a slight variation from the sodium chloride structure must be considered because there is some crystallographic evidence for less than holohedral symmetry. The probability of such a shift in atomic positions being real does not, though, seem very great. The length of the side of the unit cube (Fig. 6) is determined as:  $a = 5.214\text{A.U.}$

*Zinc Blende*,  $\text{ZnS}$ .—Zinc blende is one of the first crystals to have been studied with X-rays, and its structure has been investigated with both spectrometric and Laue photographic data.<sup>85, 86, 20, 92</sup> The atomic arrangement which is deduced from these studies gives the atoms within a unit cube  $5.42\text{A.U.}$  on a side the coördinate positions (Fig. 9):

Zinc:	000;	$\frac{1}{2}\frac{1}{2}0$ ;	$\frac{1}{2}0\frac{1}{2}$ ;	$0\frac{1}{2}\frac{1}{2}$ .
Sulfur:	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;	$\frac{3}{4}\frac{3}{4}\frac{1}{4}$ ;	$\frac{3}{4}\frac{1}{4}\frac{3}{4}$ ;	$\frac{1}{4}\frac{3}{4}\frac{3}{4}$ .

A recent measurement of powder photographs<sup>25</sup> from this crystal gives:  $a = 5.40\text{A.U.}$

*Wurtzite*,  $\text{ZnS}$ .—One very poor reflection<sup>72</sup> agrees with a "zinc oxide arrangement" (Fig. 7), but a more thorough investigation is necessary before the structure can safely be taken as established.

---

\* Communicated by Dr. Arthur L. Day, Director of the Geophysical Laboratory and Associate Editor of this JOURNAL.

† Continued from JOUR. FRANK. INST., Feb., 1923, 195, No. 2, p. 210.



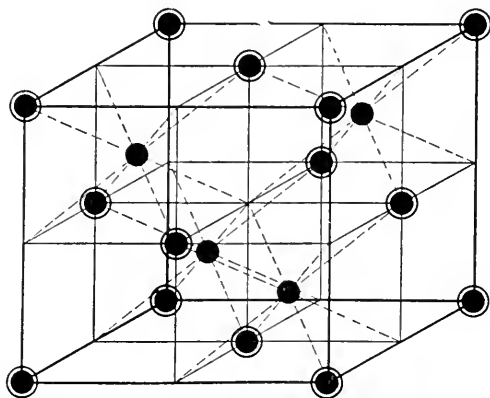
*Greenockite*,  $\text{CdS}$ .—A single reflection<sup>72</sup> appears to show that this structure also resembles that of zincite (Fig. 7).

*Strontium Selenide*,  $\text{SrSe}$ .—Powder photographs<sup>88</sup> are said to yield a "sodium chloride arrangement" (Fig. 6). The length of the side of the unit cube is given as 6.20A.U. No data have yet been published in confirmation of this assignment.

*Galena*,  $\text{PbS}$ .—It is reported, presumably on the basis of spectrometric measurements,<sup>89</sup> that this crystal has the "sodium chloride arrangement" (Fig. 6), but no data have ever appeared.

DISULFIDES, ETC.—Measurements have been made upon pyrite ( $\text{FeS}_2$ ), hauerite ( $\text{MnS}_2$ ) and cobaltite ( $\text{CoAsS}$ ), all of

FIG. 9.



The unit cube of "zinc sulfide arrangement." According to the description in the text the sulfur atoms are shown by the black circles.

which are cubic. The first has been thoroughly studied both with spectrometric and Laue photographic measurements. The manner of arrangement of the atoms in  $\text{MnS}_2$  has been accurately determined, though a satisfactory observation of the size of the unit cube is not available. Spectrographic data from cobaltite have given the size of the unit cell, but the atomic positions could not be established.

*Pyrite*,  $\text{FeS}_2$ .—Spectrometric data were early used<sup>86</sup> for an approximate placing of atoms. Though no treatment based upon space-group results has ever been published, there can be little doubt of the correctness of this structure. The unit cube is stated to be 5.38A.U. on an edge. The coördinate positions of the atoms within it are (Fig. 10):

Iron:	000; $\frac{1}{2}\frac{1}{2}0$ ; $0\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}0\frac{1}{2}$ .
Sulfur:	$uuu$ ; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$ ; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$ ; $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$ ; $\bar{u}\bar{u}\bar{u}$ ; $\frac{1}{2} - u, u + \frac{1}{2}, u$ ; $u, \frac{1}{2} - u, u + \frac{1}{2}$ ; $u + \frac{1}{2}, u, \frac{1}{2} - u$ .

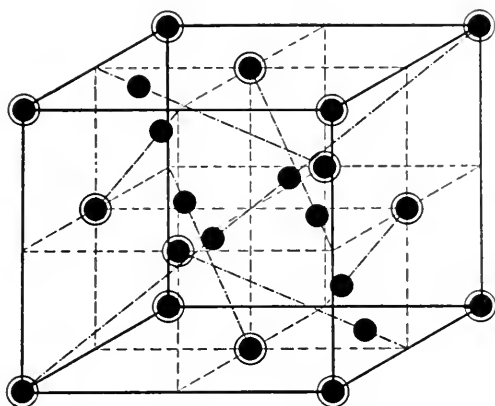


In the original assignment of structure  $u$  was made 0.4. Taking this structure as approximately right, Laue photographic data<sup>90, 91</sup> have been used to place the sulfur atoms with greater accuracy; thus  $u$  was found close to 0.388.

*Haucrite*,  $\text{MnS}_2$ .—Proceeding upon the assumption that the atomic arrangement is the same as in pyrite (Fig. 10) Laue photographic data<sup>90, 91</sup> have given  $u = 0.400$ . No measurement of the length of the side of the unit cube is recorded.

*Cobaltite*,  $\text{CoAsS}$ .—A spectrographic observation<sup>93</sup> upon a crystal of cobaltite indicates that the ratio  $m/n^3 = 4$ . From the

FIG. 10.



The unit cube of the "pyrite ( $\text{FeS}_2$ ) arrangement." The sulfur atoms are represented by the black circles.

measurements of Laue photographs it is evident that four molecules are contained within the unit cube ( $a = 5.65 \pm 0.02 \text{ A.U.}$ ) and that the corresponding space-group is  $T^4$ . The coördinate positions of the atoms within the unit are thus:

$$\text{Cobalt: } uuu; u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}; \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u; \frac{1}{2} - u, \bar{u}, u + \frac{1}{2}.$$

Arsenic and sulfur have similar arrangements in  $v$  and  $w$ . The values of these parameters— $u$ ,  $v$  and  $w$ —cannot now be defined with any certainty. If, as seems probable,  $u$  has a value close to zero, the structure is analogous to that of pyrite with one of the sulfur atoms replaced by arsenic.

#### SUMMARY OF STRUCTURES OF "INORGANIC COMPOUNDS NOT SALTS."

The structures of the crystals of this general group which have been investigated are summarized in Table III. Alloys are not included.



TABLE III.  
*Crystal Structures of Inorganic Compounds not Salts.*

Compound.	System of Symmetry.	Type of Arrangement.	Text Figure of Unit Cell.	Dimensions of Unit Cell.	Class of Determination.
CSi.....	Hexagonal	.....	.....	.....	?
H <sub>2</sub> O.....	Hexagonal	.....	.....	.....	III
Cu <sub>2</sub> O.....	Cubic	Cuprite	Fig. 5	$a = 4.26, 4.32$	IA
Ag <sub>2</sub> O.....	Cubic	Cuprite	Fig. 5	$a = 4.768, 4.69, 4.718$	IA
CuO.....	Triclinic	Modified NaCl	.....	.....	I?
BeO.....	Hexagonal	ZnO	Fig. 7	$a = 2.696; c = 4.394$	IIA
MgO.....	Cubic	NaCl	Fig. 6	$a = 4.22-4.18$	IA
CaO.....	Cubic	NaCl	Fig. 6	$a = 4.74, 4.768, 4.84$	IIA
SrO.....	Cubic	NaCl	Fig. 6	$a = 5.104$	IIA
BaO.....	Cubic	NaCl	Fig. 6	$a = 5.47, 5.496$	IIA
ZnO.....	Hexagonal	ZnO	Fig. 7	$a = 3.22; c = 5.18$	IA
CdO.....	Cubic	NaCl	Fig. 6	$a = 4.72$	IIA
NiO.....	Cubic	NaCl	Fig. 6	$a = 4.14, 4.20$	IIA
SiO <sub>2</sub> (quartz)	Hexagonal	.....	.....	.....	IIIB
TiO <sub>2</sub> (rutile)	Tetragonal	.....	.....	.....	IIIB
TiO <sub>2</sub> (anatase)	Tetragonal	.....	.....	.....	IIIB
ZrSiO <sub>4</sub> .....	Tetragonal	.....	.....	.....	IIIB
SnO <sub>2</sub> .....	Tetragonal	.....	.....	.....	IIIB
Fe <sub>2</sub> O <sub>3</sub> .....	Hexagonal	.....	.....	.....	IIIB
Al <sub>2</sub> O <sub>3</sub> .....	Hexagonal	Mn(OH) <sub>2</sub>	Fig. 8	$a = 3.34; c = 4.68$	IA
Mn(OH) <sub>2</sub> .....	Hexagonal	Mn(OH) <sub>2</sub>	Fig. 8	$a = 3.13; c = 4.75$	IA
Mg(OH) <sub>2</sub> .....	Hexagonal	NaCl	Fig. 6	$a = 5.214$	IA
MnS.....	Cubic	ZnS	Fig. 9	$a = 5.42$	IIA <sup>2</sup>
ZnS (blende)	Cubic	ZnO (?)	Fig. 7	.....	IIA <sup>2</sup>
ZnS (wurtzite)	Hexagonal	ZnO (?)	Fig. 7	.....	IIA?
CdS.....	Hexagonal	NaCl	Fig. 6	$a = 6.20$	IIA?
SrSe.....	Cubic	Pyrite	Fig. 6	$a = 5.38$	IIA
PbS.....	Cubic	Pyrite	Fig. 10	.....	IIA
FeS <sub>2</sub> (pyrite)	Cubic	Pyrite	Fig. 10	.....	IIA
MnS <sub>2</sub> (hauerite)	Cubic	Pyrite type	.....	$a = 5.65$	IA
CoAsS.....	Cubic	.....	.....	.....	IA



## HALIDES, CYANIDES, ETC.

## MONOHALIDES.

This group has been more completely studied than any other. As would be expected from the difficulty of preparing crystals of appreciable size, the data are taken for the most part from powder photographs. These data have been considered from the standpoint of space-group theory so that there can be little doubt of the essential correctness of the structure assignments. This same space-group treatment is applicable to the other cubic monohalides, those of copper, silver and thallium. The only hexagonal monohalide, silver iodide, has also been given a thorough treatment. A few more complicated monohalides have been investigated with varying degrees of completeness.

*Lithium Hydride*,  $\text{LiH}$ .—Powder photographs<sup>94</sup> show four chemical molecules within a unit cube the edge of which:  $a = 4.10\text{-A.U.}$  They are in best agreement with a "sodium chloride arrangement" (Fig. 6) of positive lithium and negative hydrogen ions.

THE ALKALI HALIDES.—Powder photographs have been prepared from all of the alkali halides. Such data form the basis for an investigation<sup>95, 96</sup> of most of the members of this group of crystals that has taken account of all possible structures. Examination has also been made of various isolated compounds, but rarely have the data been presented upon which these assignments are based. The Laue photographs which have been made from a few of these crystals may be said to agree with the results of other methods of study though a thorough treatment of them by recent procedure has not been published. The summary, which is given below, of results of structure study upon these crystals shows acceptable agreement between the different studies. In several instances the determinations of absolute dimensions, however, differ by more than the natural experimental error. A study of the sizes of these crystals which is based upon analyzed material is required before these differences can be reconciled.

*Lithium Fluoride*,  $\text{LiF}$ .—Structure:<sup>22</sup> "Sodium chloride arrangement" (Fig. 6). The length of the side of the unit cube:  $a = 4.14\text{A.U.}$  and  $a = 4.02\text{A.U.}$ <sup>65</sup>

*Lithium Chloride*,  $\text{LiCl}$ .—Structure:<sup>96</sup> "Sodium chloride arrangement" (Fig. 6). The length of the side:  $a = 5.17 \pm 0.02\text{A.U.}$



*Lithium Bromide*, LiBr.—Structure:<sup>96</sup> “Sodium chloride arrangement” (Fig. 6). The length of the side:  $a = 5.48 \pm 0.02 \text{ A.U.}$

*Lithium Iodide*, LiI.—Structure:<sup>96</sup> “Sodium chloride arrangement” (Fig. 6). The length of the side:  $a = 6.06 \pm 0.02 \text{ A.U.}$  This determination was not so satisfactory as most of the others. A couple of faint lines found upon the photographs do not agree with the structure; they are probably to be ascribed to hydration products. Likewise the calculated and observed intensities of the reflections, while not in serious disagreement with one another, are not so good as usual.

*Sodium Fluoride*, NaF.—Structure: “Sodium chloride arrangement” (Fig. 6). The length of the side of the unit cube:  $a = 4.61 \pm 0.01 \text{ A.U.}$ ,<sup>96</sup>  $4.68 \text{ A.U.}$ <sup>97</sup> and  $5.62 \text{ A.U.}$ <sup>65</sup> The last, agreeing with that of sodium chloride and unsupported by experimental data, is undoubtedly wrong.

*Sodium Chloride*, NaCl.—(Fig. 6.) The length of the side of the unit cube<sup>99, 86, 100, 98, 64</sup> is  $a = 5.628 \text{ A.U.}$  Several diagrams<sup>98, 64</sup> of Laue photographs have been published.

*Sodium Bromide*, NaBr.—Structure: “Sodium chloride arrangement” (Fig. 6). Two determinations of the length of the side give:  $a = 5.95 \pm 0.01 \text{ A.U.}$  and  $a = 6.02 \text{ A.U.}$ <sup>95, 97</sup>

*Sodium Iodide*, NaI.—Structure: “Sodium chloride arrangement” (Fig. 6). The length<sup>95, 97</sup> of the side:  $a = 6.47 \pm 0.01 \text{ A.U.}$  and  $a = 6.50 \text{ A.U.}$

*Potassium Fluoride*, KF.—Structure: “Sodium chloride arrangement” (Fig. 6). The length<sup>96, 97, 65</sup> of the side:  $a = 5.36 \pm 0.01 \text{ A.U.}$  and  $a = 5.38 \text{ A.U.}$

*Potassium Chloride*, KCl.—Structure: “Sodium chloride arrangement” (Fig. 6). The length of the side<sup>97</sup>:  $a = 6.26 \text{ A.U.}$  Diagrams<sup>98, 64</sup> of Laue photographs have been published.

*Potassium Bromide*, KBr.<sup>98, 64, 95, 97</sup>—Structure: “Sodium chloride arrangement” (Fig. 6). The length of the side:  $a = 6.59 \pm 0.02 \text{ A.U.}$  and  $a = 6.60 \text{ A.U.}$

*Potassium Iodide*, KI.—Structure: “Sodium chloride arrangement” (Fig. 6). The length<sup>95, 97, 65</sup> of the side:  $a = 7.11 \pm 0.02 \text{ A.U.}$  and  $a = 7.10 \text{ A.U.}$  A diagram of a Laue photograph has been published.<sup>101</sup>

*Rubidium Fluoride*, RbF.—In the only study that has been made,<sup>96</sup> the powder photographic data were not in sufficiently



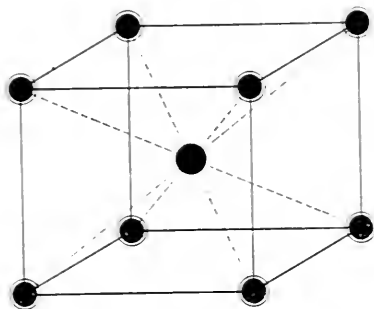
close agreement with any simple arrangement to justify an assignment of structure.

*Rubidium Chloride*,  $\text{RbCl}$ .—Structure: "Sodium chloride arrangement" (Fig. 6). The length<sup>95</sup> of the side:  $a = 6.60 \pm 0.02 \text{ A.U.}$

*Rubidium Bromide*,  $\text{RbBr}$ .—Data have not been published, but this crystal undoubtedly has the "sodium chloride arrangement" (Fig. 6). The length of the side<sup>71</sup>:  $a = 6.93 \text{ A.U.}$

*Rubidium Iodide*,  $\text{RbI}$ .—Structure: "Sodium chloride arrangement" (Fig. 6). The length<sup>95, 102</sup> of the side:  $a = 7.36$

FIG. 11.



The unit cube of the "caesium chloride arrangement." According to the description in the text the chlorine atom is shown by the black circle.

$\pm 0.02 \text{ A.U.}$  and  $a = 7.308 \text{ A.U.}$  No data have been published for the second.

*Cæsium Fluoride*,<sup>96</sup>  $\text{CsF}$ .—Structure: "Sodium chloride arrangement" (Fig. 6). The length of the side:  $a = 6.03 \pm 0.02 \text{ A.U.}$

*Cæsium Chloride*,  $\text{CsCl}$ .—An assignment of structure,<sup>103</sup> in support of which no data have been published, gives the arrangement of Fig. 11, the coördinate positions of the atoms within this unit cube being: Cæsium, 000; chlorine,  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The length of the side:  $a = 4.12 \text{ A.U.}$

*Cæsium Bromide*,  $\text{CsBr}$ .—Structure: "Cæsium chloride arrangement" (Fig. 11). The length<sup>95, 102</sup> of side:  $a = 4.30 \pm 0.01 \text{ A.U.}$  and  $a = 4.287 \text{ A.U.}$

*Cæsium Iodide*,  $\text{CsI}$ .—Structure: "Cæsium chloride arrangement" (Fig. 11). The length<sup>95, 97</sup> of the side:  $a = 4.55 \pm 0.015 \text{ A.U.}$  and  $a = 4.58 \text{ A.U.}$

THE THALLOUS HALIDES.—Unpublished powder photographs<sup>103</sup> are said to give thallos chloride the "caesium chloride arrangement."



*Thallous Chloride*,  $\text{TlCl}$ .—The length of the side of the unit cube containing a single molecule (Fig. 11):  $a = 3.85\text{A.U.}$

THE CUPROUS HALIDES.—All<sup>101</sup> of these crystals give powder diffraction data in agreement with a “zinc sulfide arrangement” (Fig. 9). It is further shown that no other simple structure is possible and that there is no experimental evidence for a complicated one. The assurance of correctness for these structures is strengthened by the fact that both determinations of copper iodide<sup>104, 105</sup> have been made by methods employing the results of the theory of space-groups.

*Cuprous Chloride*,  $\text{CuCl}$ .—Structure: “Zinc sulfide arrangement” (Fig. 9). One determination<sup>104</sup> of the length of the side gives:  $a = 5.49\text{A.U.}$ ; the other study<sup>60</sup> is described by saying that cuprous chloride is a diamond-cube of ions  $2.32\text{A.U.}$  on a side. If this is understood as a “zinc sulfide arrangement” in which the distance from copper to chlorine is  $2.32\text{A.U.}$ , the length of the side of the unit cube becomes  $5.36\text{A.U.}$  No data are published for this latter assignment.

*Cuprous Bromide*,  $\text{CuBr}$ .—Structure: “Zinc sulfide arrangement” (Fig. 9). One determination<sup>104</sup> of the length of the side gives:  $a = 5.82\text{A.U.}$ ; the other  $a = 5.75\text{A.U.}$  if the results<sup>60</sup> are interpreted as are those of the second report on cuprous chloride.

*Cuprous Iodide*,  $\text{CuI}$ .—Structure: “Zinc sulfide arrangement” (Fig. 9). One of the recorded determinations was made upon artificial crystals, the other upon natural marshite which contained some silver (a previous analysis of some of the material having shown about 1.19 per cent. silver). The length of the side determined<sup>104</sup> from powder photographs of artificially prepared copper iodide gave  $a = 6.10\text{A.U.}$  in good agreement with that calculated from the density. The spacing of the marshite<sup>105</sup> was found to be  $6.02\text{A.U.}$  Cuprous iodide has also been described<sup>60</sup> as a diamond-cube of ions  $2.63\text{A.U.}$  on a side. This again is probably intended to mean the “zinc sulfide arrangement” in which the distance between nearest unlike atoms is  $2.63\text{A.U.}$  If such is the case, the length of the side of the unit cube becomes  $6.07\text{A.U.}$

THE SILVER HALIDES.—An adequate study<sup>105, 106</sup> has been carried out only upon the low temperature form of silver iodide, for which both Laue photographic and powder data are available. Powder measurements have been made upon the others.



Silver iodide is particularly interesting because in the case with which it was assigned a cubic structure, though possessed of hexagonal symmetry, it furnishes an excellent illustration of the insufficiency of unaided powder photographs and sounds a warning of the dangers arising from a disregard of available crystallographic information.

*Silver Chloride*,  $\text{AgCl}$ .—Two reports<sup>107, 60</sup> upon silver chloride give it a "sodium chloride arrangement" (Fig. 6), the length of the side of the unit cube being stated as:  $a = 5.56\text{A.U.}$  and  $5.52\text{A.U.}$  In neither instance were any data presented.

*Silver Bromide*,  $\text{AgBr}$ .—Both determinations<sup>107, 60</sup> agree in giving silver bromide the same atomic arrangement as sodium chloride (Fig. 6) with the length of the side of the unit cube:  $a = 5.78\text{A.U.}$  No data are available for this crystal.

*Silver Iodide*,  $\text{AgI}$ .—According to two determinations<sup>107, 60</sup> based upon power data, silver iodide has a diamond-cube (meaning a zinc sulfide) arrangement with a length of side:  $a = 6.53\text{A.U.}$  Silver iodide is dimorphous, hexagonal below  $146^\circ\text{C.}$  above that cubic. It thus appears that powder photographs have been used to assign a cubic arrangement to a crystal possessed of hexagonal symmetry. This conclusion has been confirmed by the thorough treatment that has been given to this crystal with both powder and Laue photographic data.<sup>105, 106</sup> The Laue photographs prepared with single crystals of suitable size showed clearly a hexagonal character. The structure finally accepted is the "zinc oxide arrangement" (Fig. 7), the coördinate positions of the atoms being:

$$\begin{array}{ll}\text{Silver:} & \frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}. \quad (u \text{ being here taken as zero}) \\ \text{Iodine:} & \frac{1}{3}, \frac{2}{3}, u; \frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}.\end{array}$$

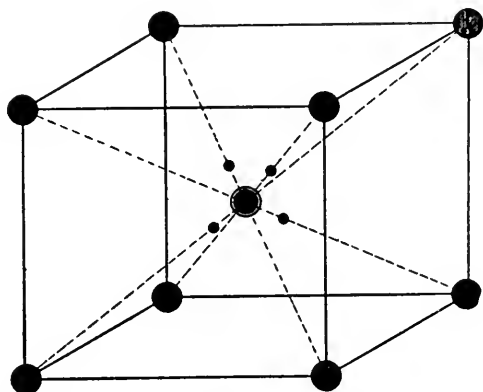
The length of the side of the unit prism was calculated as  $a = 4.59\text{A.U.}$ , its height  $c = 7.53\text{A.U.}$  corresponding to the axial ratio  $c : a = 1.639$ . The data are in best agreement with a value of  $u$  close to  $\frac{5}{8}$ . It was further shown that all but one of the lines to be expected from the assigned cubic structure coincide with lines of the correct hexagonal arrangement. The four other lines which the hexagonal structure alone contributes to the pattern are all present but so weak that they would not be detected except upon a good film. This then is a very clear example of the dangers of trying to deduce crystal structures with unaided



powder data. As a result of a powder photograph<sup>105</sup> of the high temperature (cubic) form it is concluded that the structure is of great complexity. At the time of publication of this detailed treatment of silver iodide, a similar investigation was in progress in this laboratory by E. Posnjak and the writer with optical examinations by H. E. Merwin. This incomplete work had confirmed the truly hexagonal character of the salt at ordinary temperatures and yielded Laue photographs having the same general characteristics as those published.

*Miersite*.<sup>105</sup>—Material of a composition near to  $4\text{AgI}.\text{CuI}$  has been analyzed and considered as a distinct mineral type. A

FIG. 12.



The unit cube of the atomic arrangement in the low temperature modification of ammonium chloride. In this figure the chlorine atoms are shown by the large black circles, the hydrogen atoms by the small ones. Since the position of the hydrogen atoms is indeterminable the location of these small black circles is without significance.

powder photograph showed a structure of the zinc sulfide type; consequently this mineral can be considered as a mixed crystal of silver and copper iodides.

AMMONIUM AND PHOSPHONIUM HALIDES AND SUBSTITUTED PRODUCTS.—A detailed study with both powder and Laue photographs has been made of the low temperature form of ammonium chloride. Powder data have also been obtained from the high temperature form of ammonium chloride and both forms of the bromide. Ammonium iodide has been treated with powder data and spectrometer measurements. Of the other members of this group, the simplest and probably the correct arrangement for phosphonium iodide has been deduced and a possible structure suggested for tetramethylammonium iodide.

*Ammonium Chloride*,  $\text{NH}_4\text{Cl}$ .—The low temperature modification of ammonium chloride is of interest because its structure



can be established with a high degree of certainty and because the symmetry of that atomic arrangement is at variance with the crystallographically assigned symmetry. On account of this special interest Laue photographic data<sup>108</sup> as well as powder data<sup>109</sup> have been used for a study<sup>108, 110</sup> of all possible arrangements. The atoms have the following coördinate positions within the unit cube containing a single molecule (Fig. 12):

Nitrogen:	000.
Chlorine:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .
Hydrogen:	$uuu; \bar{u}\bar{u}u; \bar{u}u\bar{u}; u\bar{u}\bar{u}$ .

The length of the side of this unit has been found<sup>109</sup> to be:  $a = 3.859 \text{ A.U.}$ ; the positions of the hydrogen atoms is indeterminable.

Powder photographic<sup>109</sup> data are said to give a "sodium chloride arrangement" of the atoms of the high temperature form of ammonium chloride. The length of the side of the unit cube containing four chemical molecules is stated to be  $6.533 \text{ A.U.}$  at  $250^\circ \text{ C.}$  The correct structure for this crystal may not be so simple as this.<sup>111</sup> If the hydrogen atoms have positions whose symmetry conforms to that of the crystal as a whole, and if there are four chemical molecules within the unit cube, the crystal symmetry can no longer be holohedral cubic. Two arrangements of the nitrogen and chlorine atoms become possible, one (I) derived from the space-groups  $T^1$  or  $T_d^1$ , the other (II) from the space-group  $T^4$ . The coördinate positions in these two cases are

(I)  $uuu; \bar{u}\bar{u}u; \bar{u}u\bar{u}, u\bar{u}\bar{u}$ , where  $u$  has a different value for  $N$  and  $Cl$ .

(II)  $uuu; u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}; \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u; \frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$ ,  $u$  being different for  $N$  and  $Cl$ . Since the powder data are in substantial agreement with the "sodium chloride arrangement," it seems necessary that  $u_N$  and  $u_{Cl}$  have such values as will make these arrangements approach closely to this grouping. In (I) it is accomplished by making  $u_N$  and  $u_{Cl}$  near to  $\frac{1}{4}$  and  $\frac{3}{4}$ ; in (II) they have values close to 0 and  $\frac{1}{2}$ . Two possible arrangements containing thirty-two molecules within the unit also can be made to approach the sodium chloride structure. There are various ways of arranging the hydrogen atoms. It will be seen that no more than an approximation to the correct atomic arrangement can now be furnished. The same is true of the high temperature

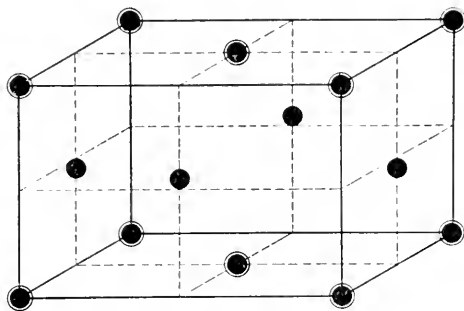


form of ammonium bromide and of the ordinary modification of ammonium iodide.

*Ammonium Bromide*,  $\text{NH}_4\text{Br}$ .—Low temperature form: <sup>109</sup> Powder photographic data from the form stable at room temperature give the body-centred structure characteristic of the ordinary form of ammonium chloride (Fig. 12). The length of the side of this unit cube containing one chemical molecule is stated as  $a = 3.988\text{A.U.}$

High temperature modification: <sup>109</sup> At  $250^\circ\text{C.}$  the powder data are said to agree with a "sodium chloride arrangement," the length of the side at this temperature being:  $a = 6.90\text{A.U.}$

FIG. 13.



The arrangement of the atoms within the unit tetragonal prism that has been assigned to crystals of phosphonium iodide. The iodine atoms are represented by black circles. The hydrogen atoms are not shown because the manner of their arrangement could not be definitely established.

For the reasons outlined under the corresponding form of ammonium chloride this determination is only approximate.

*Ammonium Iodide*,  $\text{NH}_4\text{I}$ .—Ammonium iodide stable at room temperature corresponds to the high temperature form of the other ammonium halides. Two studies have been made on the structure of this crystal, one with spectrometric measurements,<sup>112</sup> the other with powder data.<sup>109</sup> They agree in assigning to it a "sodium chloride arrangement," the length of the side of the unit being:  $a = 7.20\text{A.U.}$  and  $a = 7.199\text{A.U.}$  As already pointed out, this structure is only approximately established.

*Phosphonium Iodide*,  $\text{PH}_4\text{I}$ .—Crystals of phosphonium iodide possess tetragonal symmetry. It has been shown<sup>113</sup> that spectrographic and Laue photographic data agree with the following atomic arrangement of the phosphorus and iodine atoms:

Phosphorus:  $000; \frac{1}{2}\frac{1}{2}0.$   
 Iodine:  $0\frac{1}{2}u; \frac{1}{2}0\bar{u}.$

The dimensions of this unit tetragonal prism are found to be:



$a = 6.34\text{A.U.}$ ,  $c = 4.62\text{A.U.}$  This arrangement is shown in Fig. 13. The hydrogen atoms can have various distributions about the phosphorus atom. The results of the theory of space-groups indicate that there is no simpler arrangement which will fit these data.

*Tetramethylammonium Iodide*,  $\text{N}(\text{CH}_3)_4\text{I}$ .—Only spectrometric observations<sup>112</sup> have been made upon these crystals which likewise have tetragonal symmetry. In the original assignment of structure four carbon atoms were arranged in a tetrahedron which did not contain the nitrogen of the substituted ammonium radical. This arrangement was chemically so improbable that other possible arrangements have been investigated.<sup>111</sup> As a result it was decided that the corresponding space-group is  $D_{4h}$  and a structure was presented which placed the nitrogen atoms at the centres of tetrahedrons of carbon atoms. The single application of spectrometric measurements to so complicated a crystal cannot be taken as entirely satisfactory. Furthermore, even if the space-group assignment is correct the several arrangements that arise have not all been eliminated. For these reasons more work, both of an experimental and theoretical character, must be carried out before the atomic arrangement will be established.

MONOCYANIDES.—*Potassium cyanide* is the only crystal of this group whose structure has been investigated by X-ray methods. In a preliminary announcement spectrometer and spectrometer powder observations<sup>114</sup> are believed to show an arrangement similar to that prevailing in sodium chloride. This assignment is substantiated by a detailed treatment<sup>115</sup> based upon spectrographic and Laue photographic data. It is pointed out that if there are four chemical molecules within the unit as the data indicate, then the symmetry must be either tetrahedral or tetartohedral with an atomic arrangement built upon the same special cases that have just been discussed for the high temperature form of ammonium chloride. If the structure contains thirty-two molecules within the unit cell its symmetry can be holohedral with one of the arrangements mentioned as possibilities for ammonium chloride and treated in detail for magnesium oxide.<sup>68</sup> The centres of the cyanide groups and of the potassium atoms must approach the "sodium chloride arrangement." The two determinations place the length of the side of the unit cell

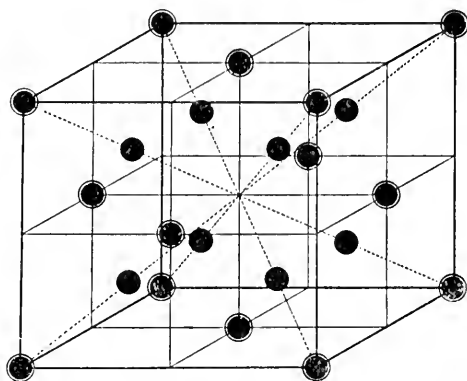


containing four chemical molecules as:  $a = 6.54 \text{ A.U.}$  and  $a = 6.55 \text{ A.U.}$

**DIHALIDES.**—Two fluorides of metals,  $\text{CaF}_2$  and  $\text{BaF}_2$ , have been investigated. Besides these cadmium iodide and the dihydrochloride of hydrazine have been studied.

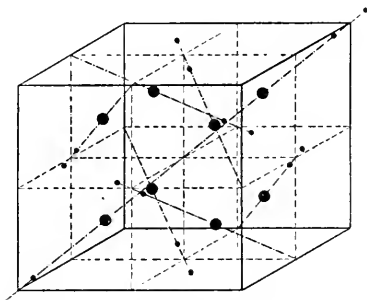
**Fluorite,  $\text{CaF}_2$ .**—The structure assigned to this crystal has been based upon spectrometric measurements.<sup>86</sup> Laue photo-

FIG. 14.



The unit cube of the "fluorite arrangement." The eight fluorine atoms within this unit are represented by black circles.

FIG. 15.



The arrangement of atoms within the unit cube of hydrazine hydrochloride ( $\text{N}_2\text{H}_6\text{Cl}_2$ ). In this modified pyrite grouping the nitrogen atoms are shown by small, the chlorine atoms by large circles. The hydrogen atoms have not been given.

graphs<sup>98</sup> also have been prepared. Four chemical molecules are contained within the unit cube (Fig. 14) with atoms in the following coördinate positions:

Calcium:  $000$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

Fluorine:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{1}{4}$ .

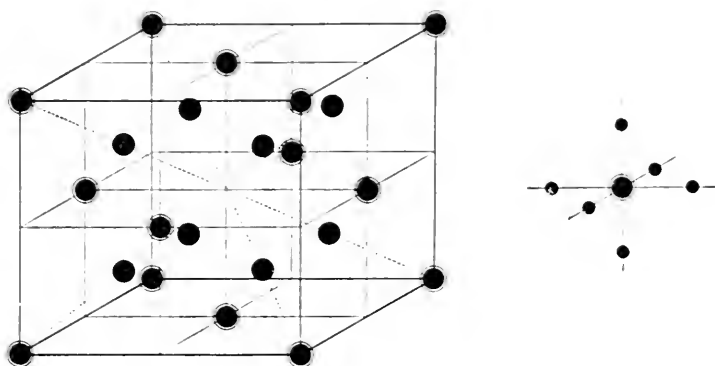
The length of the side of this unit cube has been variously stated as <sup>26, 25, 60</sup>  $5.40 \text{ A.U.}$ ,  $5.452 \text{ A.U.} \pm 0.2 \text{ per cent.}$ ,  $5.478 \text{ A.U.} \pm 0.2 \text{ per cent.}$ ,  $5.455 \text{ A.U.} \pm 0.1 \text{ per cent.}$  and  $5.49 \text{ A.U.}$  All of these except the first are based upon powder measurements.



*Barium Fluoride*,  $\text{BaF}_2$ .—Powder photographic data<sup>69</sup> are said to give the "calcium fluoride arrangement" (Fig. 14), though no data have been published. The length of the side of the unit cube is given as:  $a = 6.20\text{A.U.}$

*Cadmium Iodide*,  $\text{CdI}_2$ .—This trigonal crystal has been studied<sup>116</sup> with spectrographic and Laue photographic data. It is shown that these data agree with a hexagonal unit containing one chemical molecule. The length of the side of such a unit

FIG. 16.



The arrangement of atoms within the unit cube of crystals of the hexammonates of the nickel halides and of crystals isomorphous with ammonium chloroplatinate. In the unit cell shown in this figure nickel atoms and platinum, or isomorphous, atoms are represented by ringed circles. Six nitrogen atoms are grouped about each nickel atom and six chlorine atoms about each platinum atom after the manner of the side figure. This little figure is drawn in parallel orientation to the large unit cell.

prism is  $a = 4.24\text{A.U.}$ , its height  $c = 6.84\text{A.U.}$  The coördinate positions of the atoms (Fig. 8) are:

Cadmium: 000.

Iodine:  $\frac{1}{3}, \frac{2}{3}, u$ ;  $\frac{2}{3}, \frac{1}{3}, \bar{u}$ .

The parameter  $u$  for iodine is found to be close to 0.75. Except for a different value of  $u$  this is the pyrochroite arrangement.

*Hydrazine Dihydrochloride*,  $\text{N}_2\text{H}_6\text{Cl}_2$ .—The structure of this cubic crystal has been studied<sup>117</sup> with the aid of spectrographic and Laue photographic data. It is shown that in the unit cube which is  $7.89\text{A.U.}$  on a side and contains four chemical molecules, the atoms must have the arrangement expressed by the following coördinates (Fig. 15):

Chlorine atoms:  $uuu$ ;  $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$ ;  $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$ ;  $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$ ;  $\bar{u}\bar{u}\bar{u}$ ;  $\frac{1}{2} - u, u + \frac{1}{2}, u$ ;  $u, \frac{1}{2} - u, u + \frac{1}{2}$ ;  $u + \frac{1}{2}, u, \frac{1}{2} - u$ .

Nitrogen atoms: a similar arrangement in  $v$ .

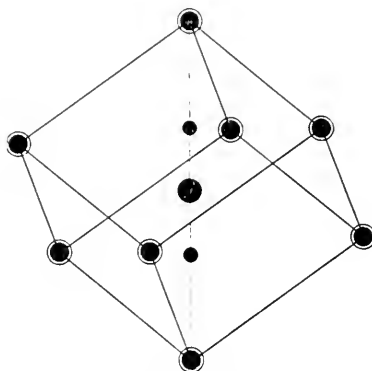
Hydrogen atoms: the twenty-four generally equivalent positions of the space-group  $T_h^6$ .



The parameter  $u$  for chlorine is 0.27+; the most probable value of the similar parameter  $\tau$  for the nitrogen atoms is taken to be around 0.04.

AMMONATES OF THE DIHALIDES.—The three hexammonates of the nickel halides ( $\text{NiX}_2 \cdot 6\text{NH}_3$ ) are the only members of this group which have been investigated. Their structures<sup>118</sup> have been studied with spectrographic and Laue photographic data.

FIG. 17.



The arrangement of the atoms within the unit rhombohedron of caesium dichloriodide. No attempt is made to show the true shape of this rhombohedron. The iodine atoms are indicated by large, the chlorine atoms by small black circles.

The arrangement of the atoms within the unit cube which contains four molecules (Fig. 16) is the following:

Nickel:  $\cdot 000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}.$   
 Halogen:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}.$   
 Nitrogen:  $u00; \bar{u}00; u\frac{1}{2}\frac{1}{2}; \bar{u}\frac{1}{2}\frac{1}{2};$   
 $0u0; 0\bar{u}0; \frac{1}{2}u\frac{1}{2}; \frac{1}{2}\bar{u}\frac{1}{2};$   
 $00u; 00\bar{u}; \frac{1}{2}\frac{1}{2}u; \frac{1}{2}\frac{1}{2}\bar{u};$   
 $u + \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2} - u, \frac{1}{2}, 0; \frac{1}{2}, u + \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2} - u, 0;$   
 $u + \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2} - u, 0, \frac{1}{2}; 0, u + \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2} - u, \frac{1}{2};$   
 $\frac{1}{2}, 0, u + \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2} - u; 0, \frac{1}{2}, u + \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2} - u.$

Hydrogen: there are several different arrangements possible depending upon the symmetry assumed for these crystals but they all agree in permitting three of the hydrogen atoms to be associated with each nitrogen atom to form an ammonia group.

*Nickel Chloride Hexammonate*,  $\text{NiCl}_2 \cdot 6\text{NH}_3$ .—The length of the side<sup>118</sup> of the unit cube is:  $a = 10.09\text{A.U.}$  It is shown that  $u$  for nitrogen has a value between 0.227 and 0.245. A simple announcement,<sup>119</sup> without any data, agrees with these results.

*Nickel Bromide Hexammonate*,  $\text{NiBr}_2 \cdot 6\text{NH}_3$ .—The length of the side<sup>119</sup> of the unit cube is:  $a = 10.48\text{A.U.}$  No estimation was made of  $u$ .

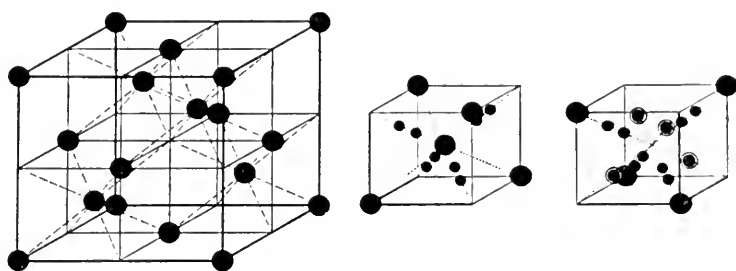


*Nickel Iodide Hexammonate*,  $\text{NiI}_2 \cdot 6\text{NH}_3$ .—The length of the side of the <sup>119</sup> unit cube is:  $a = 11.01 \text{ A.U.}$  The nitrogen atoms could not be so accurately placed as in the chloride, but it was shown that  $u$  must lie between 0.20 and 0.25, probably near to 0.24.

**POLYHALIDES.**—Diffraction measurements have been recorded upon caesium dichloriodide and potassium triiodide.

*Cæsium Dichloriodide*,  $\text{CsCl}_2\text{I}$ .—This crystal is crystallographically reported as dimorphous, rhombohedral and orthorhombic. Repeated trials produced only the rhombohedral modifi-

FIG. 18.



The arrangement of the atoms within the unit cube of crystals of potassium zinc cyanide. The position of the eight zinc atoms is shown in the large cube. The two sub-units indicate the positions of the other atoms within alternate little cubes of the unit cell. Because they could not be distinguished both the carbon and nitrogen atoms are shown by little black circles.

cation and twins which simulated orthorhombic symmetry. Both spectrographic and Laue photographic data <sup>120</sup> were used to assign a structure, but no detailed use was made of the results of the theory of space-groups. Nevertheless, it is probable that the structure is correct. The coördinate positions within the unit rhombohedron (Fig. 17) are the following:

Cæsium:	000;	or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .
Iodine:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ;	or 000.
Chlorine:	uuu; $\bar{u}\bar{u}\bar{u}$ .	

The angle between the axes of this unit is  $70^\circ 42'$ ; its length of side:  $a = 5.46 \text{ A.U.}$  The parameter  $u$  lies between 0.312 and 0.317. Unfortunately it was impossible to decide between the alternative arrangements of the caesium and iodine atoms because of their probably similar scattering powers.

*Potassium Triiodide*,  $\text{KI}_3$ .—A cubic structure has been given <sup>121</sup> to this crystal by a modified spectrometer method. In view of its apparently well-established monoclinic symmetry, a further consideration of this work is not justified, particularly in the absence of experimental data.

(To be concluded.)



**Selective Reflection of  $\lambda$  2536 by Mercury Vapor.** R. W. WOOD. (*Phil. Mag.*, Dec., 1922.)—"In earlier papers it was shown that there appear to be two types of selective reflection of radiation which is very nearly in synchronism with the free period of the mercury molecule at the 2536 absorption line. One type is due to the abnormally low value of the refractive index of the vapor on the short wave-length side of the line. The change of refractive index at the boundary quartz-Hg vapor is greater than the change for a boundary quartz-vacuum, since the refractive index is less than unity, consequently we have strong reflexion for radiations immediately adjacent to the absorption line on the short wave-length side. The high value of the refractive index of the vapor for radiations slightly greater than that of the absorption line, makes the change of index at the boundary small, consequently the reflection for these radiations is very feeble. This was shown by reflecting the light of  $\lambda = 2536$  from a quartz arc operated at high temperature (2536 broad and strongly reversed) from the inner surface of a flat prismatic quartz plate which was sealed to a quartz bulb containing mercury vapor at a pressure of several atmospheres. The reflected light was photographed with a quartz spectrograph, and only the short wave-length half of the reversed 2536 line was found on the plate." An additional experiment with a more homogeneous source of light confirmed the result, but it seemed desirable to try it with an even more homogeneous light. The light from a water-cooled quartz mercury arc was sent to a quartz monochromator. From this a strong beam of 2536 light fell on a mercury resonance lamp at room temperature. The monochromatic 2536 light from this impinged on the surface of a prismatic quartz plate which formed the end of a quartz tube containing mercury vapor. From the plate the light was reflected to a photographic plate. The tube was used cold or heated to  $400^{\circ}$  C. "The image reflected from the plate was much denser in the case of the exposure with the bulb hot." "The reflecting power of the plate when backed by dense mercury vapor (density corresponding to  $400^{\circ}$ ) was between 3.5 and 4 times as great as the normal reflecting power of the quartz for the wave-length in question." G. F. S.

**Anomalies in the Thermal Expansion of Glass.** P. LAFON. (*Comptes Rendus*.)—These anomalies came to light in the study of enamels. The differential method of Chevenard was used in which a comparison is made of the expansion of the specimen of glass with that of a rod of steel of the same length. At about  $500^{\circ}$  C. a smaller dilation of the glass than at lower temperatures shows itself. When the glass cools down this anomaly does not appear. At about  $600^{\circ}$  C. glass ceases to expand and at higher temperatures contracts. This is a reversible phenomenon. It is difficult to make the author's statements agree with his curves.

G. F. S.



## NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

### RECOMMENDED MINIMUM REQUIREMENTS FOR SMALL DWELLING CONSTRUCTION.<sup>1</sup>

INVESTIGATIONS by a Congressional Committee during 1919 and 1920 disclosed that existing building laws, through variations and inconsistencies of their provisions and through unduly restrictive or expensive requirements, were operating to prevent needed activity in the building industry. That these conditions might be remedied, a committee of experienced architects and engineers was organized by Secretary Hoover, to investigate building practice and code requirements and to prepare standard building regulations based on the latest and best information, which might be recommended to cities and states adopting or revising building codes.

The first report of this committee presents recommendations for the construction of one- and two-family dwellings having exterior walls of solid or hollow masonry, concrete, and frame, the latter including veneer and stucco surfaces.

In order that its recommendations might have sound bases of information and opinion, the committee obtained the coöperation of nearly one hundred architectural and engineering societies, builders' exchanges, and industrial organizations producing building materials. Special questions also were referred to large groups of individual engineers, architects, building officials, to the Bureau of Standards, and to others whose experience qualified them to discuss such subjects. Tentative recommendations were drafted and submitted widely for discussion and criticism by those interested in the work, and the final report reflects the influence of this consideration.

The committee recommends that building codes permit 8-inch solid brick and 6-inch solid concrete walls for 2½- and 3-story dwellings accommodating not more than two families each; that 8-inch hollow building tile, hollow concrete block, or hollow walls of brick (all rolok) shall not exceed 20 feet in height to the

---

\* Communicated by the Director.

<sup>1</sup> Abstract of a report by the Building Code Committee of the Department of Commerce, published for the committee by the Bureau of Standards.



gables; and that frame construction be limited to  $2\frac{1}{2}$  stories. Metal lath and plaster on wood studs properly firestopped is approved for party and division walls, but at least every alternate wall in row houses must be 8-inch solid brick or concrete or 12-inch hollow building tile, concrete block, or hollow wall of brick.

Requirements for quality of hollow masonry units agree fairly well with present practice, but those for brick are somewhat below the medium grade established by the American Society for Testing Materials. The report recommends revised working stresses for timber used in dwellings, based on investigations of the U. S. Forest Products Laboratory. Live loads to be required as bases for design are 40 pounds per square foot for floors of wood, and 30 for those of monolithic type, or of solid or ribbed slabs. Foundation walls of brick are required to be 12 inches thick for excavated enclosures, and similar concrete walls shall be as thick as the walls they support but not less than 8 inches. Special hollow building tile 12 inches thick is permitted for foundation walls of frame buildings. Detailed recommendations are given for firestopping and chimney construction, also for treatment of built-in garages.

The recommended requirements are followed by a lengthy appendix containing explanatory material and much educational matter for the guidance of builders, with particular reference to the merits of 8-inch and 12-inch masonry walls, use of lumber, stucco construction, plastering, and other important subjects.

---

**Protection of Wood from Moisture.** (Tech. Notes, Forest Products Laboratory.)—The porosity of wood makes it susceptible to marked changes by changes in moisture content. Investigations were made to determine the best protecting coatings. Linseed oil though highly valued was found to be of little use. The best coating is the aluminum leaf which was developed in the Forest Products Laboratory as a coating for airplane propellers, but this can be applied only to large unbroken surfaces. Asphalt and pitch paints are efficient, but the color is often objectionable. No way has yet been found to apply over these paints lighter colored materials. Cellulose lacquers have some advantages. For temporary protection vaselin smeared over varnish or a heavy coat of paraffin is satisfactory. These cannot be used on surfaces subject to wear. H. L.



NOTES FROM THE RESEARCH LABORATORY,  
EASTMAN KODAK COMPANY.\*

QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE. II.<sup>1</sup>

By L. Silberstein and A. P. H. Trivelli.

AN account is given of some further experimental tests of the theory proposed in the first paper by Silberstein (*Phil. Mag.*, 1922, 44, p. 257), and some new formulæ are deduced from the fundamental one given in that paper, especially a formula which takes care of the finite breadth of a size-class of grains. Svedberg and Andersson's independent work is mentioned as corroborating the theory. The principles of clumps as units used in the previous paper is defended. Finally, two tables of experimental results obtained in the laboratory, and of theoretical values are given which show, on the whole, an excellent agreement between the facts and the light dart or light quantum theory of photographic exposure.

ASTRONOMICAL PHOTOGRAPHIC PHOTOMETRY AND THE  
PURKINJE EFFECT. II.<sup>2</sup>

By F. E. Ross.

THE four methods in use for the photographic photometry of stars are outlined and the principles underlying each are pointed out. The turbidity method depends on the increase of size of image with intensity. The Greenwich formula connecting the diameter of the image with the magnitude of the star is shown to fail for images less than  $50\mu$  in diameter and a new formula which holds for all cases is suggested:  $\sqrt{(d+h)} = a + b \log I$ , where  $a$ ,  $b$ , and  $h$  are constants. On the assumption that the growth of the image is due to diffuse scattering and reflection of light formulæ for the intensity of this light at any distance from the edge are deduced and section of images are given which show both theoretical and actual equiluminous surfaces. However, it is found by experiment that the rate of growth or turbidity is not constant but increases with the intensity, for instance, from

\* Communicated by the Director.

<sup>1</sup> Communication No. 149 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, November, 1922, p. 956.

<sup>2</sup> Communication No. 150 from the Research Laboratory of the Eastman Kodak Company and published in *Astrophys. J.*, December, 1922, p. 345.



9 to  $12\mu$  when the intensity is multiplied three hundred fold. This effect is of importance in accurate measurements, since, if it is not allowed for, deduced relative magnitudes will vary with the time of exposure. Data are also given showing marked variations of turbidity with the kind of plate, and with the telescope used, but if the optical system is well corrected the optical turbidity should be negligible. The probable error of this method is about 0.01 for very sharp images but may be reduced considerably by using plates of greater turbidity and with small inherent irregularity. In the densitometric method which involves the measurement of out-of-focus images, the probable error is small except that due to inherent plate irregularities, so the more these are reduced the greater will be the relative accuracy of this method. The variation of turbidity with wave-length, the photographic Purkinje effect, is of great importance. The results obtained are reviewed, but because of the complexity of the effect no general conclusions can as yet be given. An explanation is suggested for Abney's discovery that for some plates the least gradation is for the wave-length of maximum sensitivity.

Transmission of some photographic plates to white, blue, green, and red light is given. While Bloch and Renwick have found that the absorption is not exponential, for very thin films the law (Bouguer's) may hold, at least approximately.

Photographic turbidity for spectrum lines is found to be the same as for circular images of the same width.

#### ON THE SPECTRUM OF NEUTRAL HELIUM.<sup>3</sup>

By L. Silberstein.

A QUANTUM theory of the spectrum lines of neutral helium is given, based on the assumption that there is *no appreciable interaction* between the two electrons revolving around the nucleus. The spectrum formula yielded by this assumption is a superposition of two Balmerian ones and is shown to represent with sufficient accuracy over eighty (out of the 110) spectrum lines of neutral helium, hitherto unaccounted for theoretically. The probability of the agreement being merely fortuitous is estimated to be exceedingly small. Possible applications of the principle (of no interaction between interatomic electrons) to other atoms, especially to lithium, is hinted at.

---

<sup>3</sup> Communication No. 156 from the Research Laboratory of the Eastman Kodak Company and published in *Astrophys. J.*, September, 1922, p. 119.



## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

### THE ODOROUS CONSTITUENTS OF APPLES. II. EVIDENCE OF THE PRESENCE OF GERANIOL.<sup>1</sup>

By Frederick B. Power and Victor K. Chesnut.

[ABSTRACT.]

AN examination of McIntosh apples has confirmed the results of a previous investigation that the odorous constituents of the apple consist chiefly of amyl esters, and it has also afforded further information respecting the substance which imparts to some apples a distinctly rose-like odor. Although the proportion of this substance, even in the McIntosh apple, is extremely small, it has nevertheless been possible to show with some degree of certainty that it consists of the aliphatic terpene alcohol geraniol,  $C_{10}H_{18}O$ .

The evidence for this conclusion may be adduced from the fact that by the hydrolysis of the esters of the apple a product was obtained which possessed, in addition to the odor of amyl alcohol, a rose-like fragrance, and that by the oxidation of this product it yielded, besides valeric acid, a substance which had the characteristic odor and other properties of the aldehyde citral. At the same time the formation in very small quantities of the further oxidation products of geraniol or citral, which are acetone and levulinic acid, was indicated. It is probable that geraniol, either in the free state or in the form of esters, is contained in varying quantities in all varieties of the apple, although to the greatest extent in those which possess its distinctive odor.

### SIGNIFICANCE OF WHEAT HAIRS IN MICROSCOPICAL EXAMINATION OF FLOUR.<sup>2</sup>

By George L. Keenan.

[ABSTRACT.]

DATA obtained on experimental samples of flour indicate the possibility of making an interesting classification based on the wheat-hair count alone. Of course, the number of hairs or hair fragments from the brush of the wheat grain might differ mate-

---

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *J. Amer. Chem. Soc.*, **44** (December, 1922): 2938.

<sup>2</sup> Issued as *U. S. Dept. Agr. Bul.* 1130, Jan. 26, 1923.



rially, according to the variety of wheat used and the milling operations employed. Nevertheless, an examination of a large number of samples representing a great variety of milling practices indicates that flours made from purified middlings material show a low hair count, while flours containing lower-grade mill stocks show a higher hair count.

---

### CANNED SPINACH AS A SOURCE OF BOTULISM.<sup>3</sup>

By Ruth B. Edmondson, Charles Thom and L. T. Giltner.

[ABSTRACT.]

THE Microbiological Laboratory of the Bureau of Chemistry obtained for study 653 cans of the pack of spinach responsible for the outbreak of botulism at Kendallville, Indiana. Cans found free from evidence of spoilage, as determined by inspection, were free from evidence of bacterial activity, as determined by culture. Cans showing swell carried active contaminations with bacteria or were pronounced examples of chemical corrosion. In so far as the samples received from commercial sources were concerned, inspection by persons familiar with canned spinach proved to be a safe basis for passing or condemning these samples. Exactly the same results were obtained in the investigation of a number of separate brands in 1921.

In cans inoculated for experimental purposes, resealed and incubated, individual discordant examples were encountered. Three out of sixty-four cans reached a stage of toxin formation sufficient to kill guinea-pigs before gas or odor or both had developed sufficiently to make possible their removal by inspection. Among large numbers of cans handled under widely different storage conditions, the occurrence of an occasional can in which toxicity has reached the danger point before gas or swell is detectable is clearly a possibility in dealing with spinach. Hence careful inspection before opening should be followed by actual re cooking of this product as it comes from the can.

Incubation under observation at the factory is recommended, with such precautions in identifying the lot or batch as will insure the detection of undercooked lots of cans from any cause.

---

<sup>3</sup> Published in *Am. Food Journal*, 18 (January, 1923) : 33.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

### MESOTHORIUM.

By Herman Schlundt.

AMONG the thirty-odd radioactive elements, mesothorium, the first product of thorium, ranks next to radium in importance. Like radium, its disintegration products emit the three types of radiation that are characteristic of radioactive substances and that are known as alpha, beta, and gamma rays. Mesothorium decays at least 250 times faster than radium, and hence in the pure state its activity, weight for weight, would greatly exceed that of radium. Although itself rayless, its first product, which is rapidly formed after mesothorium has been separated, gives a powerful beta and gamma radiation; the alpha radiation of freshly prepared radium attains a maximum within a month, whereas that of mesothorium increases comparatively slowly, and reaches its high point during the fifth year after separation. Mesothorium preparations therefore must be "aged" before their full alpha-ray effect is realized in luminous products.

In the radium series one member, radium C, is mainly responsible for the gamma radiation. In the mesothorium series two members—the first product, mesothorium 2, and the final radioactive member, thorium D—emit gamma rays, those from thorium D being the most penetrating rays known. The maximum gamma activity is attained during the fourth year after separation, and its value is approximately 2.5 times that due to the mesothorium 2 present at the time. Consequently, during the first years of separation, notwithstanding the comparatively rapid decay of mesothorium, its preparations maintain a higher gamma-ray activity than an equivalent quantity of radium. Mesothorium may thus serve as a substitute for radium, both in luminous compounds of radium and for therapeutic purposes.

Further details, based on experimental work by the writer in laboratories of the U. S. Bureau of Mines, the Welsbach Company, and the University of Missouri, covering a period of several years, are presented in Technical Paper 265.

---

\* Communicated by the Director.



## COAL ANALYSES FROM TWENTY-FIVE LABORATORIES COMPARED.

By A. C. Fieldner, H. M. Cooper, and F. D. Osgood.

THE Bureau of Mines has recently conducted a study of results obtained in analyzing similar samples of coal and coke by twenty-five laboratories throughout the country, in comparison with results obtained in the bureau's coal laboratory at Pittsburgh. The purpose of this work was primarily to obtain a comparison of the methods of coal analysis used by the laboratories of the American Gas Association. Standard samples were prepared in the Bureau of Mines' coal laboratory at Pittsburgh, and portions sent to each laboratory, and to twelve commercial laboratories not affiliated with the association.

The results obtained indicate a closer application of the A.S.T.M. methods outlined in the *Gas Chemists' Handbook* than in previous comparisons. It is essential that all of the laboratories of the Gas Association, as well as other coal laboratories, use the standard methods in their coal work to ensure accurate analysis of the fuel. Attention is called to the following points:

1. Dry air must be circulated through the moisture oven at a sufficient rate to change the volume of the oven three to four times per minute.

2. The best results are obtained for the determination of volatile matter when a 10 c.c. capsule type crucible with a well-fitting cover is used. The electric furnace is superior to the Meker burner for consistent work.

3. The use of open burners is likely to give high results with manufactured gas in the sulphur determination. Sulphur determined from bomb washing will invariably run low, varying in proportion to the amount of sulphur present.

4. More attention should be given to the proper application of corrections for acidity, radiation, and sulphur in the calorimeter determination. The calorimeter bomb should have an inner surface of platinum, gold, porcelain enamel, or other material not attacked by nitric or sulphuric acids or other products of combustion.

Nickel linings should not be used if results checking within A.S.T.M. limits are desired. Further details are given in Serial 2432 of the bureau.



**METALLURGICAL POSSIBILITIES OF THE DESCLOIZITE  
ORES AT GOODSPRINGS, NEVADA.**

By H. A. Doerner.

For the past three or four years attention has been attracted to the deposits of lead vanadate in the Goodsprings, Nevada, district. Some ore running as high as 9 per cent.  $V_2O_5$  has been produced, but most of it runs from 0.5 to 3 per cent. Only a little ore, and that of the richer sort, has been shipped.

It has been estimated that the district is capable of producing twenty-five tons per day of ore averaging from 2 per cent. to 3 per cent.  $V_2O_5$ . Since ore of that grade and character will not stand the cost of shipment or of chemical refining, a concentrating mill is essential to any plan for the exploitation of the deposits.

Experiments on table concentration of the ore indicate that ordinary classification and tabling of the ore and treatment of the slimes on a special canvas table will extract at least 70 per cent. of the lead and vanadium content and yield a concentrate containing 10 per cent.  $V_2O_5$  and over 30 per cent. Pb.

No practical method, either mechanical or chemical, was found which would reduce the loss of metals in the slimes below 15 per cent. of the total amount.

The 10 per cent.  $V_2O_5$  concentrate will stand the costs of shipment and the extraction of the lead and vanadium, but on account of its unusual nature, there may be difficulty in finding a satisfactory market. If such is the case, the concentrate may be profitably refined by smelting to remove the lead and reduction of the vanadium bearing slag to ferro alloy by means of silicon; or the lead may be separated by a reducing caustic fusion and the vanadium leached from the slag and precipitated as vanadic acid. The latter method is to be preferred on account of the uniformly high extraction and the high-grade product. Further details are given in a recent report issued by the bureau.

---

**EFFECT OF CARTRIDGE DIAMETER ON THE STRENGTH AND  
SENSITIVENESS OF CERTAIN HIGH EXPLOSIVES.**

By Spencer P. Howell and J. E. Crawshaw.

ONE of the most important problems in mental mining, tunneling or quarrying, is the most economical method of bringing down the ore or rock. The two factors having great influence in determining this are drilling and blasting costs.



The bureau's attention has been called to the lack of definite data on the effect of cartridge diameter on the strength and sensitiveness of high explosives. This information is especially valuable to the user of explosives as it assists him in determining what diameter of borehole is most economical.

The Bureau of Mines, in coöperation with the Institute of Makers of Explosives, has carried out a series of tests to show the effect of cartridge diameter on the strength and sensitiveness of certain high explosives.

The explosives chosen for the tests are those very extensively used in metal mining, tunneling and quarrying, namely, 40 per cent. strength L. F. gelatin dynamite, 60 per cent. strength L. F. gelatin dynamite and 40 per cent. strength ammonia dynamite.

The tests carried out have shown conclusively,

(1) That both the rate of detonation and sensitiveness to explosion by influence increase with the increase in diameter of cartridge.

(2) That gelatin dynamites rapidly decrease in sensitiveness to detonation and explosion by influence on aging while the ammonia dynamite was very little affected.

(3) That the insensitiveness of gelatin dynamites to detonation and explosion by influence on aging proceeds more rapidly the smaller the diameter of cartridge.

(4) That the insensitiveness to detonation and explosion by influence proceeds more rapidly with 60 per cent. strength L. F. gelatin dynamite than with 40 per cent. strength L. F. gelatin dynamite. Further information will be found in the report on this subject recently published by the bureau.

---

**A New Amplifier of Sounds.** L. GAUMONT. (*Comptes Rendus.*)—Many amplifiers of sound distort it without mercy. It is claimed that the following device is free from this defect. The vibrating part is a cone of fine silk fabric around which is wound a spiral of fine aluminum wire in one or more layers. The angle of the cone is  $90^\circ$ . This is introduced into the space between the pole pieces of an electromagnet which have the same angle. The cone fits over one of these. When telephonic currents are sent through the aluminum wire there are forces exerted upon the latter by reason of the interaction between its magnetic field and that of the electromagnet. Since the spiral has no natural period of its own, it does not reproduce the sound with distortion. Great distinctness is claimed as well as great intensity.

G. F. S.



# THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, February 21, 1923.*)

HALL OF THE FRANKLIN INSTITUTE,  
PHILADELPHIA, February 21, 1923.

MR. BENJAMIN FRANKLIN, *Temporary Chairman.*

The Board of Managers submitted its report. The report recorded the election to membership of:

T. Wistar Brown, 3rd, Esq., Attorney, 230 Chestnut Street, Philadelphia, Pennsylvania.

John Tracy Lay, Esq., B.S., Research Assistant in Physics, University of Pennsylvania, Philadelphia, Pennsylvania.

William C. Melcher, Jr., Esq., William Cramp and Sons Ship and Engine Building Company, Philadelphia, Pennsylvania.

Honorable William C. Sproul, Esq., B.S., President General, Refractories Company, 1512 Chestnut Street, Philadelphia, Pennsylvania;

lectures before the Sections as follows:

"Principles of Electrical Vibration Instruments" by

A. E. Kennelly, D.Sc.,

Professor of Electrical Engineering,

Harvard University and Massachusetts Institute  
of Technology

Cambridge, Massachusetts;

"Physics and Chemistry of Plant Life" by

Rodney H. True, Ph.D.,

Professor of Botany,

University of Pennsylvania,

Philadelphia, Pennsylvania;

"Motion Picture Photography for the Amateur" by

C. E. K. Mees, D.Sc.,

Director of Research Laboratory,

Eastman Kodak Company,

Rochester, New York;

"Tidal and Current Work of the Coast and Geodetic Survey" by

Lieutenant Commander G. T. Rude,

Chief, Division of Tides and Currents,

U. S. Coast and Geodetic Survey,

Washington, D. C.

and a lecture before the Stated Meeting, January 17, 1923, by

E. A. Eckhardt, Ph.D.,

Physicist,

Bureau of Standards,

Washington, D. C.

on "Building Acoustics";



also the following additions to the library, 47 bound volumes, 20 unbound volumes and 95 pamphlets.

The Board of Managers also transmitted the following memorandum and resolution:

"The Board of Trustees of The Franklin Institute have instructed the Fidelity Trust Company to sell a lot on Belfield Avenue in the City of Philadelphia, included in the bequest of William H. Wahl to the Institute. In order that the title to this lot may be properly passed, it is requested that the following resolution be adopted by the Institute:

*"Resolved*, That the title to premises known as Lot No. 28 on the Plan of Lots of the Walnut Lane Land Association situate on Belfield Avenue in the Twenty-second Ward of the City of Philadelphia, more particularly described in Deed dated March 10, 1892, recorded in Philadelphia in Deed Book T. G. No. 100, page 560 (except 20 ft. off the rear end previously sold), said Lot being a part of the devise to The Franklin Institute for the Promotion of the Mechanic Arts under the Will of William H. Wahl, deceased, and known as the 'John H. Wahl Fund,' be conveyed to the Trustees of The Franklin Institute in accordance with Article I, Section I, of the By-Laws of the Institute. And the President and Secretary are hereby authorized and directed to execute the Deed for the same."

Doctor Hoadley moved that the resolution, as presented, be adopted. The Motion was duly seconded and passed unanimously.

A report of progress was presented by the Committee on Science and the Arts.

The Chairman then announced that the next business of the meeting would be the presentation of the Elliott Cresson Medal to Dr. Lee deForest and recognized Mr. Charles E. Bonine, who said:

*"Mr. Chairman:* The invention of the three-electrode vacuum tube for the purpose of amplifying minute electrical currents and pressures, called by its inventor the Audion, and variously known as the electron amplifier, thermionic amplifier, three-electrode bulb, etc., which is the specific invention under consideration, is one of the most important ever made in the field of the electrical transmission of intelligence and through its development has worked a profound revolution in the art of radio communication.

"In consideration of this invention, marking as it does a signal advance in the art of electrical transmission of intelligence, The Franklin Institute awards the Elliott Cresson Medal to Dr. Lee deForest of Jersey City, New Jersey.

"Mr. Chairman, I take pleasure in presenting Dr. Lee deForest."

The Chairman presented the Medal, accompanying Certificate and Report to Doctor deForest who, in accepting the award, said:

*"Mr. Chairman, Members of The Franklin Institute, Ladies and Gentlemen:* It is useless for me to attempt to express in words my appreciation of the great honor conferred on me to-night by the Award of the Elliott Cresson Medal of the Institute.

"I can but regard this award, not as a personal one, to the inventor of the Audion, but rather as a tribute to the device itself, as an instrumentality



which has already proven itself as of very great and genuine value to mankind; and one which promises in the future to confer even greater benefits than those which it has heretofore given.

"Two years ago I presented before the Institute, a paper on the Audion. In this, I dwelt at some length upon the utility of the invention during the great War. To-night, I would speak, very briefly, upon the value of the Audion in Peace, in directly aiding in the cause of continued Peace.

"Although as early as 1907 I had foreseen the coming day when the Radio Telephone would be used in nation-wide, world-wide broadcasting, and although I had, in season and out of season, preached the benefits to our people which such broadcasting would bring, yet I did not foresee, two years ago, that the great wave of popularity and appreciation of this new medium was so nearly upon us.

"Nothing since the early days of the discoveries has so appealed to the imagination of a Nation. No other medium in man's history has demonstrated its unique power for uniting far-separated sections of a great country, for causing to become acquainted dwellers in distant districts—from north to south, from east to west. More than the newspaper, more than the postal service, this mighty service of hearing the spoken voice in greeting, the public address, the sermon, the lecture, the musical program—is actively uniting in a bond of common fellowship, common acquaintanceship, as no other conceivable instrumentality can accomplish.

"I predict that, as an educational medium, the Radio Telephone Broadcast will, in time, prove second in importance only to the Public School.

"As methods of transmission and reception become perfected, the benefits which we already see so clearly in the United States, will become international in scope. Already we see a closer interlinkage between the people of Canada and ourselves, due to the broadcasting idea. Soon these benefits will extend to Europe, and between the peoples of the old world, always heretofore strangers, enemies because strangers and personally unacquainted. When, night after night, the citizens of foreign lands will hear the friendly words, the music, the songs from across strange frontiers, then gradually will the feelings of enmity and suspicion, based chiefly on distances and ignorance of each other, change to understanding and good will.

"Thus, I maintain, the Radio Broadcast is destined to prove one of the most potent powers for the abolition of War in the history of the World.

"That the Audion as detector, amplifier, and transmitter has made possible this widespread introduction and popularity of Radio Broadcasting is, I consider, an adequate reason why it has been singled out to be honored by this Award, which you have seen fit to bestow here to-night."

After the transaction of the above business the meeting became a joint one with the Philadelphia Section of the American Society of Civil Engineers and the Chairman requested Professor William Easby, Jr., President, to preside.

The paper of the evening on "The Main Piers of the Bridge over the Delaware River between Philadelphia and Camden" was presented by Mr. Clement E. Chase, C.E., Principal Assistant Engineer, and Mr. M. B. Case, B.Sc., Senior Resident Engineer, Delaware River Bridge Joint Commission.



Mr. Chase described the construction of the granite and concrete piers upon which the great main towers of the bridge are to be supported. Details of the construction of the two largest pneumatic caissons ever used in a bridge foundation were given. The fundamental changes embodied in the design of these caissons based on experience with previous large caissons was pointed out. Recognition of the necessity for reducing the risks to the compressed air workers was reflected in provision of emergency refuge chamber, use of air locks, large enough to hold an entire shift and in the safety requirements of the specifications.

Mr. Case described the building of the complete pneumatic caissons ready for sinking, in one of the large shipyards, and contrasted the situation with other conditions frequently encountered in the building of bridges. The enormous area of the caissons made it desirable to keep the unit pressures at the cutting edge as small as possible during sinking to avoid excessive warping and racking stresses in the caisson structure. Procedure to accomplish this condition was described as was the ample equipment of hoisting shafts and air locks with convenient disposal of muck into barges alongside. Medical examinations and attention for compressed air workers was outlined with records of results accomplished. The plant and methods used for the construction of massive granite ashlar masonry was described.

Lantern slides were used to illustrate the subject.

The Chairman extended the thanks of the meeting to the speakers.

Adjourned.

R. B. OWENS,  
*Secretary.*

---

## COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of the Stated Meeting held Wednesday,  
February 7, 1923.)*

HALL OF THE FRANKLIN INSTITUTE,  
PHILADELPHIA, February 7, 1923.

DR. JAMES BARNES *in the Chair.*

Mr. W. H. Fulweiler was unanimously elected Chairman for the year 1923. The following reports were presented for final action:

No. 2763: Universal Measuring Machine. Final reading of report was held over until the March meeting.

No. 2785: Maxon Pre-mix Burner. The Certificate of Merit to Mr. Harry R. Maxon, of Muncie, Indiana.

No. 2798: Adjustable Hinge. Final reading of report was held over until the March meeting.

The following report was presented for first reading:

No. 2806: Literature.

R. B. OWENS,  
*Secretary.*



## SECTIONS.

*Electrical Section.*—A meeting of the Section was held on Thursday evening, January 11, 1923, at eight o'clock, with Mr. W. C. L. Eglin in the Chair.

A. E. Kennelly, D.Sc., Professor of Electrical Engineering, Harvard University and Massachusetts Institute of Technology, Cambridge, Massachusetts, presented the paper of the evening on "The Principles of Electrical Vibration Instruments."

These instruments are not only important from the practical standpoint, owing to their extensive every-day use, but their working theory bears remarkable analogies to alternating electric current theory. Some of these analogies are already known, but use is made of the motional-impedance circle for analyzing the behavior of these instruments comparatively. The principles of electrical vibration instruments, therefore, commend themselves to the notice of both mechanical engineers and electrical engineers.

The subject was fully illustrated by lantern slides.

After discussion of the subject by Dr. Carl Hering, Dr. W. R. Wright and others, a rising vote of thanks was extended to the speaker and the meeting adjourned.

T. R. PARRISH,  
*Acting Secretary.*

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, January 25, 1923, at eight o'clock, with Dr. Joseph S. Hepburn in the Chair. The minutes of the previous meeting were approved as published.

Rodney H. True, Ph.D., Professor of Botany in the University of Pennsylvania, delivered an address on "The Physics and Chemistry of Plant Life." The relationship of osmotic pressure to plant nutrition and growth was described. The communication was discussed at length. On motion of Dr. Thomas D. Cope, a vote of thanks was extended to Doctor True.

The meeting then adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

*Sections of Physics and Chemistry and Photography and Microscopy.*—A meeting of the Sections was held in the Hall of the Institute on Thursday evening, February 1, 1923, at eight o'clock, with Dr. H. J. M. Creighton in the Chair. The minutes of the previous meeting were read and approved.

C. E. K. Mees, Sc.D., Director of the Research Laboratory of the Eastman Kodak Company, Rochester, New York, presented a communication on "Motion Picture Photography for the Amateur." A description was given of a process using special, narrow-width film, very small pictures, the direct production of positives by reversal during development, and special apparatus for taking and projecting. The lecture was illustrated by means of lantern slides and a demonstration of the process from taking the picture to projecting it on the screen.

The communication was discussed at length; a vote of thanks was extended to Doctor Mees; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*



*Mechanical and Engineering Section.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, February 8, 1923, at eight o'clock, with Mr. Benjamin Franklin in the Chair.

The paper of the evening, entitled "Tidal and Current Work of the Coast and Geodetic Survey," was presented by Lieutenant Commander G. T. Rude, Chief, Division of Tides and Currents, U. S. Coast and Geodetic Survey, Washington, D. C.

The speaker gave an outline of the activities of the Coast and Geodetic Survey in tidal and current work, with special reference to recent investigations in the subject of wind-driven currents.

A non-mathematical explanation was given of the forces governing the making of the tides and currents and the different types of tides and currents were explained.

A brief description was given of the instruments and methods employed in the observation and prediction of tides and currents.

The paper, which was fully illustrated with lantern slides, dealt with the relation and importance of tides and currents to the work of the engineer, mariner and scientist.

After a short discussion a vote of thanks was extended to the speaker and the meeting adjourned.

T. R. PARRISH,  
*Acting Secretary.*

*Mining and Metallurgical Section.*—A joint meeting of the Section and the Philadelphia Chapter, American Society for Steel Treating, was held in the Hall of the Institute on Thursday evening, February 15, 1923, at eight o'clock, with Mr. G. H. Clamer in the Chair.

Walter Rosenhain, D.Sc., F.R.S., Superintendent, Metallurgy Department, The National Physical Laboratory, Teddington, England, presented a paper on "The Structure and Constitution of Alloys." The speaker emphasized the increasing importance of full detailed knowledge of the internal structure and constitution of alloys and reviewed the methods of studying structure and constitution which have been recently developed and some of the more important results obtained. The methods discussed included those relating to the thermal study of alloys by means of heating and cooling curves and their interpretation. He indicated, however, the importance of microscopic examination of alloys in various states obtained by special methods of preparation, including prolonged annealing at carefully controlled temperatures, very gradual cooling and quenching from accurately known temperatures. The application of these methods to the fundamentally important problem of determining the solubility of metals in one another in the solid state and to the study of ternary and other complex alloys, was described with special reference to alloys of aluminum whose structure, constitution and properties have recently been investigated in the lecturer's laboratory.

The subject was illustrated by lantern slides.

After an interesting discussion by the Chairman and others, a vote of thanks was extended to the speaker.

Adjourned.

T. R. PARRISH,  
*Acting Secretary.*



## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, February 14, 1923.)*

#### LIFE MEMBERSHIP.

HON. WILLIAM C. SPROUL, 117 South Sixteenth Street, Philadelphia, Pennsylvania.

#### RESIDENT MEMBERS.

MR. T. WISTAR BROWN, 3RD, 230 Chestnut Street, Philadelphia, Pennsylvania.  
MR. JOHN TRACY LAY, Assistant in Research, Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania.  
MR. WILLIAM C. MELCHER, JR., in care of I. P. Morris Department, William Cramp and Sons Ship and Engine Building Company, Philadelphia, Pennsylvania.

#### CHANGES OF ADDRESS.

MR. A. W. BERRESFORD, 303 Hotel Astor, Milwaukee, Wisconsin.  
MR. JONATHAN JONES, P. O. Box 1593, Pittsburgh, Pennsylvania.  
DR. HUGO LIEBER, 19 West 44th Street, New York City, New York.  
MR. PERCY MCGEORGE, 711 Bullitt Building, Philadelphia, Pennsylvania.  
MR. HORACE E. MOORE, Chester Heights, Pennsylvania.  
MR. JOHN STONE STONE, 3942 Alameda Street, San Diego, California.  
E. R. WADLEIGH, ESQ., Federal Fuel Distributor, 718 18th Street, Washington, D. C.

---

## NECROLOGY.

MR. CLARENCE S. BEMENT, 3907 Spruce Street, Philadelphia, Pennsylvania.

---

## LIBRARY NOTES.

### PURCHASES.

American Annual of Photography, Vol. 37, 1923. 1922.  
American Gas Association, Second and Third Annual Conventions, 9 vols. 1920-21.  
Brassey's Naval and Shipping Annual. 1923.  
CRESSWELL, ERNEST J. J.—Sponges. n. d.  
FRANKLIN, BENJAMIN.—Philosophical and Miscellaneous Papers. 1787.  
GREENISH, HENRY G.—Microscopical Examination of Foods and Drugs. Ed. 3. 1923.  
HETZEL, FREDERIC V.—Belt Conveyors and Belt Elevators. 1922.  
HEWITT, J. T.—Synthetic Coloring Matters: Dyestuffs Derived from Pyridine, Quinoline, Acridene and Xanthene. 1922.  
LIDDELL, DONALD M., ed.—Handbook of Chemical Engineering, 2 vols. 1922.  
Society of Chemical Industry, Reports of the Progress of Applied Chemistry, Vol. 6. 1921.  
World Almanac and Book of Facts for 1923.



## GIFTS.

- Abrasive Company, Booklet of Borolon Polishing Grain. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Adelphi College, Catalogue 1921-22. Brooklyn, New York. (From the College.)
- Adriance Machine Works, Incorporated, Adriance Horning and Wiring Presses. Brooklyn, New York, 1922. (From the Works.)
- Agnes Scott College, Catalogue 1921-22. Decatur, Georgia. (From the College.)
- Albany College, Catalogue 1922. Albany, Oregon. (From the College.)
- Albion College, Catalogue 1921-22. Albion, Michigan. (From the College.)
- Albright College, Catalogue 1922. Myerstown, Pennsylvania. (From the College.)
- American Coke and Chemical Company, Roberts Coke Ovens. Chicago, Illinois, 1922. (From the Company.)
- American International College, Catalogue 1922-23. Springfield, Massachusetts. (From the College.)
- Amherst College, Catalogue 1922-23. Amherst, Massachusetts. (From the College.)
- Anderson Foundry and Machine Company, Catalogue of Anderson Oil Engines. Anderson, Indiana, 1923. (From the Company.)
- Arizona Bureau of Mines, Bulletins 1-3, 5, 11, 12, 14, 16, 17, 19, 20, 22, 23, 25, 26, 29, 35-37, 39-41, 43-46, 48, 49, 59, 62, 63, 68, 72, 78, 79, 81, 82, 86, 91, 99, 104-106, 113-117, inclusive. Tucson, Arizona. (From the Bureau.)
- Atlantic Christian College, Catalogue 1922. Wilson, North Carolina. (From the College.)
- Augsburg Seminary, Catalogue 1921-22. Minneapolis, Minnesota. (From the Seminary.)
- Augustana College and Normal School, Catalogue 1922. Sioux Falls, South Dakota. (From the College.)
- Augustana College and Theological Seminary, Catalogue 1921-22. Rock Island, Illinois. (From the College.)
- Aurora College, Catalogue 1922. Aurora, Illinois. (From the College.)
- Austin College, Catalogue 1922-23. Sherman, Texas. (From the College.)
- Bacharach Industrial Instrument Company, Folder of Pamphlets on Indicators and Gauges. Pittsburgh, Pennsylvania, no date. (From the Company.)
- Bailey Meter Company, Bailey Meters, Bulletin No. 33. Cleveland, Ohio, 1922. (From the Company.)
- Baker University, Catalogue 1921-22. Baldwin City, Kansas. (From the University.)
- Baldwin-Wallace College, Catalogue 1921-22. Berea, Ohio. (From the College.)
- Bates College, Annual Catalogue 1922-23. Lewiston, Maine. (From the College.)
- Beaumont, R. H., Company, Bulletin 58, Hoist for Coke, Coal, Ashes, etc. Philadelphia, Pennsylvania, no date. (From the Company.)



- Belden Manufacturing Company, Beldenamcl Magnet Wire. Chicago, Illinois, no date. (From the Company.)
- Beloit College, Catalogue 1921-22. Beloit, Wisconsin. (From the College.)
- Berea College, Catalogue 1922. Berea, Kentucky. (From the College.)
- Bethany College, Catalogue 1922-23. Bethany, West Virginia. (From the College.)
- Bethel College, Catalogue 1922-23. Newton, Kansas. (From the College.)
- Binks Spray Equipment Company, Bulletin No. 4-D, Sprarite Cooling Pond Equipment. Chicago, Illinois, 1922. (From the Company.)
- Black and Decker Manufacturing Company, Portable Electric Tools and Shop Equipment. Baltimore, Maryland, 1922. (From the Company.)
- Blue Ridge College, Catalogue 1921-22. New Windsor, Maryland. (From the College.)
- Bodine Electric Company, Catalogue of Bodine Motors. Chicago, Illinois, 1922. (From the Company.)
- Boston College, Catalogue 1922. Chestnut Hill, Massachusetts. (From the College.)
- Boston Gear Works, Boston Gears, Catalogue 41. Boston, Massachusetts, 1922. (From the Works.)
- Boston University, Catalogue 1921-22. Boston, Massachusetts. (From the University.)
- Bowdoin College, Catalogue 1922-23. Brunswick, Maine. (From the College.)
- Bridgeport Brass Company, Brass Pipe and Piping, Bulletin No. 15. Bridgeport, Connecticut, 1922. (From the Company.)
- Bridgewater College, Catalogue 1922. Bridgewater, Virginia. (From the College.)
- Brill, J. G., Company, Catalogue No. 266, Light-weight Cars. Philadelphia, Pennsylvania, no date. (From the Company.)
- British Portland Cement Research Association, Viscosity of Raw Material Slurry Used in the Manufacture of Portland Cement. London, England, 1922. (From the Association.)
- British Scientific Instrument Research Association, Annual Report for the Year 1921-22. London, England, 1922. (From the Association.)
- Brown Brothers and Company, Railways of France. New York City, New York, 1922. (From the Company.)
- Brown and Sharpe Manufacturing Company, Brown and Sharpe Screw Machines. Providence, Rhode Island, 1922. (From the Company.)
- Brown University, Catalogue 1921. Providence, Rhode Island. (From the University.)
- Bryn Mawr College, Calendar, 1922. Bryn Mawr, Pennsylvania. (From the College.)
- Bucknell University, Catalogue 1921-22. Lewisburg, Pennsylvania. (From the University.)
- Butler College, Catalogue 1921-22. Indianapolis, Indiana. (From the College.)
- Canadian Department of Mines, Report for the Fiscal Year Ending March 31, 1922, and Memoirs 129 and 132. Ottawa, Canada, 1922. (From the Department.)



- Canada Minister of Public Works, Report for 1922. Ottawa, Canada, 1922. (From the Department.)
- Canisius College, Catalogue 1922-23. Buffalo, New York. (From the College.)
- Carrier Engineering Corporation, Booklet of Ejector Processing Cabinets. Newark, New Jersey, 1922. (From the Corporation.)
- Carroll College, Catalogue 1921-22. Waukesha, Wisconsin. (From the College.)
- Central College, Catalogue 1922. Fayette, Missouri. (From the College.)
- Central College, Catalogue 1921-22. Pella, Iowa. (From the College.)
- Centre College, Catalogue 1921-22. Danville, Kentucky. (From the College.)
- Chicago Pneumatic Tool Company, Pneumatic Tools. Chicago, Illinois, no date. (From the Company.)
- Christian University, Catalogue 1922. Fort Worth, Texas. (From the University.)
- Coe College, Catalogue 1921-22. Cedar Rapids, Iowa. (From the College.)
- Coen Company, Incorporated, Coen System of Mechanical Oil Burning. San Francisco, California, 1922. (From the Company.)
- Colby College, Catalogue 1922-23. Waterville, Maine. (From the College.)
- College of Emporia, Catalogue 1922-23. Emporia, Kansas. (From the College.)
- College of Puget Sound, Catalogue 1922. Tacoma, Washington. (From the College.)
- College of William and Mary, Catalogue 1921-22. Williamsburg, Virginia. (From the College.)
- College of Wooster, Catalogue 1921-22. Wooster, Ohio. (From the College.)
- Colorado Department of Mines, Oil-shale, an Historical, Technical and Economic Study by Martin J. Gavin. Denver, Colorado, 1922. (From the Department.)
- Colorado Iron Works Company, Drying of Fine Materials. Denver, Colorado. (From the Company.)
- Concordia College, Catalogue 1920-21. Moorhead, Minnesota. (From the College.)
- Connecticut College, Catalogue 1921-22. New London, Connecticut. (From the College.)
- Crankless Engines (Aus.) Proprietary, Limited, Handbook of the Crankless Engine. Melbourne, Australia, 1922. (From the Company.)
- Dakota Wesleyan University, Catalogue 1921-22. Mitchell, South Dakota. (From the University.)
- Defiance College, Catalogue 1922. Defiance, Ohio. (From the College.)
- De Paul University, Catalogue 1922. Chicago, Illinois. (From the University.)
- DePauw University, Catalogue 1921-22. Greencastle, Indiana. (From the University.)
- Drury College, Catalogue 1921-22. Springfield, Missouri. (From the College.)
- Earlham College, Catalogue 1921-22. Earlham, Indiana. (From the College.)
- Electric Appliance Company, Catalogue R57, Radio Supplied of Quality. Chicago, Illinois, no date. (From the Company.)
- Ellsworth College, Catalogue 1922-23. Iowa Falls, Iowa. (From the College.)
- Elmira College, Catalogue 1922-23. Elmira, New York. (From the College.)
- Elon College, Catalogue 1922. Elon College, North Carolina. (From the College.)



- Emory University, Catalogue for 1922-23. Atlanta, Georgia. (From the University.)
- Empire Radio Corporation, Booklet of Empire Radio Equipment. New York City, New York, 1922. (From the Corporation.)
- Eureka College, Catalogue 1922. Eureka, Illinois. (From the College.)
- Evansville College, Catalogues 1921-22 and 1922-23. Evansville, Indiana. (From the College.)
- Fairmount College, Catalogue 1921-22. Wichita, Kansas. (From the College.)
- Federated Engineers Development Corporation, Booklet on Labor Saving. Jersey City, New Jersey, 1922. (From the Corporation.)
- Findlay College, Catalogue 1922-23. Findlay, Ohio. (From the College.)
- Florida State College for Women, Catalogue 1922. Tallahassee, Florida. (From the College.)
- Fordham University, Catalogue 1922. Fordham, New York. (From the University.)
- Franklin and Marshall College, Catalogue 1921-22. Lancaster, Pennsylvania. (From the College.)
- Friends University, Catalogue 1921-22. Wichita, Kansas. (From the University.)
- General Chemical Company, Hard-n-Tyte Engineering Service. New York City, New York, 1922. (From the Company.)
- Geneva College, Catalogue 1922-23. Beaver Falls, Pennsylvania. (From the College.)
- Geneva Metal Wheel Company, Catalogue 16. Geneva, Ohio. (From the Company.)
- Georgetown College, Catalogue 1921-22. Georgetown, Kentucky. (From the College.)
- George Washington University, Catalogue 1922. Washington, District of Columbia. (From the University.)
- Gonzaga University, Catalogue 1921-22. Spokane, Washington. (From the University.)
- Goshen College, Annual Catalogue 1922. Goshen, Indiana. (From the College.)
- Goucher College, Catalogue 1922-23. Baltimore, Maryland. (From the College.)
- Grand Island College, Catalogue 1922-23. Grand Island, Nebraska. (From the College.)
- Greenville College, Catalogue 1922. Greenville, Illinois. (From the College.)
- Grether Fire Equipment Company, Grether Hand Electric Searchlights and Booklet of Protection and Safety Devices. Dayton, Ohio, 1922. (From the Company.)
- Grinnell College, Catalogue 1922. Grinnell, Iowa. (From the College.)
- Grove City College, Catalogue 1922. Grove City, Pennsylvania. (From the College.)
- Hamilton College, 1922 Annual Catalogue. Clinton, New York. (From the College.)
- Hamline University, Catalogue 1921-22. Saint Paul, Minnesota. (From the University.)



- Hampden-Sidney College, Catalogue 1921-22. Hampden-Sidney, Virginia. (From the College.)
- Hanover College, Catalogue 1921-22. Hanover, Indiana. (From the College.)
- Harris, Samuel, and Company, Catalogue No. 40. Chicago, Illinois, 1922. (From the Company.)
- Hastings College, Catalogue 1921-22. Hastings, Nebraska. (From the College.)
- Hiergesell Brothers, Catalogue "A" of Thermometers and Hydrometers. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Hiram College, Catalogue 1921-22. Hiram, Ohio. (From the College.)
- Holy Cross College, Catalogue 1921-22. Worcester, Massachusetts. (From the College.)
- Hood College, Catalogue 1921-22. Frederick, Maryland. (From the College.)
- Hope College, Catalogue 1921-22. Holland, Michigan. (From the College.)
- Howard College, Catalogue 1922. Birmingham, Alabama. (From the College.)
- Hunter College, Catalogue 1922-23. New York City, New York. (From the College.)
- Huron College, Catalogue 1922-23. Huron, South Dakota. (From the College.)
- Idaho Department of Mines, Seventeenth and Twentieth Annual Reports. Boise, Idaho, 1915 and 1918. (From the Department.)
- Illinois Geological Survey, Bulletins 19 to 26, 30, 33-37 and 39-44. Urbana, Illinois. (From the State Geologist.)
- India Department of Meteorology, Report of Meteorology in Mysore for 1921. Bangalore, India, 1922. (From the Department.)
- India Department of Posts and Telegraphs, Annual Report 1921-22. Delhi, India, 1922. (From the Department.)
- Indiana Central College, Catalogue 1922. Indianapolis, Indiana. (From the College.)
- Institute of Metals, Journal, Name-Subject Index to vols. i-xxv, 1909-21. London, England, 1922. (From the Institute.)
- Institution of Civil Engineers, Minutes of Proceedings, vol. ccxiii, 1921-22, Part 1. London, England, 1922. (From the Institution.)
- Institution of Naval Architects, Transactions, vol. 64. London, England, 1922. (From the Institution.)
- Iron and Steel Institute, Journal, vol. cvi. London, England, 1922. (From the Institute.)
- James Millikin University, Catalogue 1921-22. Decatur, Illinois. (From the University.)
- Jamestown College, Catalogue 1922-23. Jamestown, North Dakota. (From the College.)
- Jefferson College, Catalogue 1921-22. Convent, Louisiana. (From the College.)
- John B. Stetson University, Catalogue 1921-22. DeLand, Florida. (From the University.)
- Juniata College, Catalogue 1921-22. Huntingdon, Pennsylvania. (From the College.)
- Kalamazoo College, Catalogue 1921-22. Kalamazoo, Michigan. (From the College.)



- Kansas Geological Survey, Bulletins 1, 4, 5 and 6. Topeka, Kansas, 1913. (From the University of Kansas.)
- Kansas Wesleyan University, Catalogue 1922. Salina, Kansas. (From the University.)
- Kenyon College, Catalogue 1921-22. Gambier, Ohio. (From the College.)
- Kindt-Collins Company, Catalogue of Pattern Shop Supplies and Equipment. Cleveland, Ohio, no date. (From the Company.)
- Kuhlman Electric Company, Kuhlman Transformers. Bay City, Michigan, no date. (From the Company.)
- Laclede-Christy, Stokers. St. Louis, Missouri, no date. (From the Company.)
- Lake Erie College, Catalogue 1921-22. Painesville, Ohio. (From the College.)
- Lake Forest College, Catalogue 1921-22. Lake Forest, Illinois. (From the College.)
- Lawrence College, Catalogue 1921-22. Appleton, Wisconsin. (From the College.)
- Lebanon Valley College, Catalogue 1922. Annville, Pennsylvania. (From the College.)
- LeBlond, R. K., Machine Tool Company, Universal Tool Room Grinders, LeBlond Lathes and Multi-cut Lathes. Cincinnati, Ohio, 1922. (From the Company.)
- Lees-Bradner Company, Gear Grinding. Cleveland, Ohio. (From the Company.)
- Link-Belt Company, Catalogue 400. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Lombard College, Catalogue 1922-23. Galesburg, Illinois. (From the College.)
- Louisiana State University, Catalogue 1922. Baton Rouge, Louisiana. (From the University.)
- Loyola College, Catalogue 1921-22. Los Angeles, California. (From the College.)
- Luther College, Catalogue 1921-22. Decorah, Iowa. (From the College.)
- Lynchburg College, Catalogue 1921-22. Lynchburg, Virginia. (From the College.)
- McAlear Manufacturing Company, Catalogue No. 27. Chicago, Illinois, 1923. (From the Company.)
- Macalester College, Catalogue 1922. Saint Paul, Minnesota. (From the College.)
- Maine Public Utilities Commission, Seventh Annual Report. Waterville, Maine, 1922. (From the Commissioners.)
- Manchester Association of Engineers, Transactions 1921-22. Manchester, England, 1922. (From the Association.)
- Marietta College, Catalogue 1922-23. Marietta, Ohio. (From the College.)
- Massachusetts Institute of Technology, Courses of Study and Subjects of Instruction. Cambridge, Massachusetts, 1922. (From the Institute.)
- Mercer University, Catalogue 1922-23. Macon, Georgia. (From the University.)
- Miami University, Catalogue 1921-22. Oxford, Ohio. (From the University.)
- Middlebury College, Catalogue 1922-23. Middlebury, Vermont. (From the College.)



- Milligan College, Catalogue 1922-23. Johnson City, Tennessee. (From the College.)
- Milliken Brothers Manufacturing Company, Catalogue No. 16, Milliken Radio Towers. New York City, New York, 1922. (From the Company.)
- Mills College, Catalogue 1922-23. Oakland, California. (From the College.)
- Milwaukee-Downer College, Catalogue 1922-23. Milwaukee, Wisconsin. (From the College.)
- Mitchell Engineering Company, A Way to Reduce Polishing and Buffing Costs. Springfield, Ohio, 1922. (From the Company.)
- Modern Electric and Machine Company, Modern Piston Specification. Indianapolis, Indiana, no date. (From the Company.)
- Modern Engineering Company, Welding, Cutting, Carbon Burning and Lead Burning Pamphlet. St. Louis, Missouri, no date. (From the Company.)
- Monmouth College, Sixty-sixth Annual Catalogue, 1922. Monmouth, Illinois, 1922. (From the College.)
- Montana Wesleyan College, Catalogue 1922-23. Helena, Montana. (From the College.)
- Morningside College, Catalogue 1921-22. Sioux City, Iowa. (From the College.)
- Mount Saint Mary's College, 114th Annual Catalogue 1921-22. Emmitsburg, Maryland. (From the College.)
- Muskingum College, Catalogue 1921-22. New Concord, Ohio. (From the College.)
- Nebraska State Railway Commission, Fourteenth Annual Report, to the Governor. Lincoln, Nebraska, 1921. (From the Commissioners.)
- Nebraska Wesleyan University, Catalogue 1921-22. University Place, Nebraska. (From the University.)
- Nevada Department of Mines, Biennial Report 1919-20. Carson City, Nevada. (From the Department.)
- New York Public Service Commission, Abstracts of Reports of Corporations, Fourteenth Annual Report. Albany, New York, 1922. (From the Commissioners.)
- New York State Department of Labor, Annual Report of Commissioner of Labor. Albany, New York, 1913. (From the Department.)
- New York University, Catalogue for 1921-22. New York City, New York. (From the University.)
- North-Western College, Catalogue 1921-22. Naperville, Illinois. (From the College.)
- Northwestern University, Annual Catalogue 1921-22. Chicago, Illinois. (From the University.)
- Norwich University, Catalogue 1921-22. Northfield, Vermont. (From the University.)
- North Dakota Department of Mines, Third Annual Report. Bismarck, North Dakota, 1921. (From the Department.)
- Nuttall, R. D., Company, Nuttall Industrial Helical Gears. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Occidental College, Catalogue 1922. Los Angeles, California. (From the College.)



- Oglethorpe University, Catalogue 1922. Oglethorpe University, Georgia. (From the University.)
- Ohio State University, Catalogue 1922-23. Columbus, Ohio. (From the University.)
- Oklahoma Agricultural and Mechanical College, Catalogue 1921-22. Stillwater, Oklahoma. (From the College.)
- Oliver Machinery Company, Catalogue of Oliver Machinery. Grand Rapids, Michigan, 1922. (From the Company.)
- Ouachita College, Catalogue 1922. Arkadelphia, Arkansas. (From the College.)
- Palmer College, Catalogue 1922-23. Albany, Missouri. (From the College.)
- Park College, Catalogue 1922-23. Parkville, Missouri. (From the College.)
- Parks-Cramer Company, Industrial Heating by Oil Circulation. Boston, Massachusetts, 1922. (From the Company.)
- Patterson, W. W., Company, Blocks, Catalogue 22. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Penn College, Catalogue 1921-22. Oskaloosa, Iowa. (From the College.)
- Pennsylvania College of Gettysburg, Catalogue 1921. Gettysburg, Pennsylvania. (From the College.)
- Pennsylvania College for Women, Catalogue 1922-23. Pittsburgh, Pennsylvania. (From the College.)
- Pennsylvania State College, Catalogue 1921-22. State College, Pennsylvania. (From the College.)
- Phillips University, Catalogue 1922. Enid, Oklahoma. (From the University.)
- Piedmont College, Catalogue 1921-22. Demorest, Georgia. (From the College.)
- Pratt Institute, 1922-23 Catalogues from Schools of Library Science, Fine and Applied Arts, Household Science and Arts and Science and Technology. Brooklyn, New York. (From the Institute.)
- Presbyterian College of South Carolina, Catalogue 1921-22. Clinton, South Carolina. (From the College.)
- Protectometer Company, Storing Coal Safely. Jersey City, New Jersey, 1922. (From the Company.)
- Purdue University, Annual Catalogue 1921-22. Lafayette, Indiana. (From the University.)
- Radcliffe College, Catalogue 1922-23. Cambridge, Massachusetts. (From the College.)
- Radio Specialty Company, Catalogue No. 8 of Rasco Products. New York City, New York, 1923. (From the Company.)
- Randolph-Macon College, Catalogue 1921-22. Ashland, Virginia. (From the College.)
- Randolph-Macon Woman's College, Catalogue 1921-22. Lynchburg, Virginia. (From the College.)
- Ransome and Marles Bearing Company, Limited, Catalogue of Ball and Roller Bearings. Newark-on-Trent, England, 1922. (From the Company.)
- Reed College, Catalogue 1922-23. Portland, Oregon. (From the College.)
- Redmanol Chemical Products Company, A Popular Exposition of the Scientific Merits of Redmanol. Chicago, Illinois, 1922. (From the Company.)



- Rhode Island Public Utilities Commission, Tenth Annual Report. Providence, Rhode Island, 1922. (From the Commissioners.)
- Rhode Island State College, Catalogue 1922. Kingston, Rhode Island. (From the College.)
- Rice Institute, Catalogue 1922. Houston, Texas. (From the Institute.)
- Ripon College, Catalogue 1922. Ripon, Wisconsin. (From the College.)
- Roanoke College, Catalogue 1921-22. Salem, Virginia. (From the College.)
- Rockford College, Annual Catalogue 1922-23. Rockford, Illinois. (From the College.)
- Rollins College, Catalogue 1922. Winter Park, Florida. (From the College.)
- Rome Brass and Copper Company, Bulletin No. 1, Brass and Copper. Rome, New York, 1922. (From the Company.)
- Roots, P. H., and F. M., Company, Bulletin No. 118, Engineering Tables. Connersville, Indiana, 1922. (From the Company.)
- Roto Company, Roto Tube Cleaners. Hartford, Connecticut, no date. (From the Company.)
- Royal Academy of Sciences, Proceeding of the Section of Sciences, vol. xxi, Parts 1 to 10 and Jaarboek for 1918 and 1919. Amsterdam, Holland. (From the Academy.)
- Saint Anselm's College, Catalogue 1921-22. Manchester, New Hampshire. (From the College.)
- St. Bernard College, Catalogue 1922. St. Bernard, Alabama. (From the College.)
- Saint Francis College, Catalogue 1922-23. Brooklyn, New York. (From the College.)
- Saint John's College, Catalogue 1921-22. Annapolis, Maryland. (From the College.)
- Saint Joseph's College, Catalogue 1921-22. Philadelphia, Pennsylvania. (From the College.)
- Saint Lawrence University, Catalogue 1922-23. Canton, New York. (From the University.)
- St. Louis Car Company, Catalogue 101, Car Seats. St. Louis, Missouri, 1922. (From the Company.)
- St. Martin's College, Catalogue 1921-22. Lacey, Washington. (From the College.)
- Saint Olaf College, Catalogue 1920-21. Northfield, Minnesota. (From the College.)
- Semet-Solvay Company, Catalogue of Coke and Gas Plants. Syracuse, New York, 1922. (From the Company.)
- Seton Hall College, Catalogue 1921-22. South Orange, New Jersey. (From the College.)
- Shreve, Samuel H., A Treatise on the Strength of Bridges and Roofs. New York City, New York, 1877. (From Mr. Charles A. Beck.)
- Shurtleff College, Catalogue 1921-22. Alton, Illinois. (From the College.)
- Simmons College, Catalogue 1921-22. Abilene, Texas. (From the College.)
- Sioux Falls College, Catalogue 1922. Sioux Falls, South Dakota. (From the College.)



- Smithsonian Institution, Report of the Secretary for the Year Ending June 30, 1922. Washington, District of Columbia. (From the Institution.)
- South Dakota Board of Railroad Commissioners, Thirty-third Annual Report. Pierre, South Dakota, 1922. (From the Commissioners.)
- South Dakota Department of Geology, Annual Report, 1920-22. Vermilion, South Dakota. (From the State Geologist.)
- South Dakota Department of Mines, Twenty-eighth to Thirty-first Annual Reports, Inclusive. Pierre, South Dakota, 1917 to 1921. (From the Department.)
- South Dakota State College of Agriculture and Mechanic Arts, Catalogue 1922-23. Brookings, South Dakota. (From the College.)
- Southwestern College, Catalogue 1921-22. Winfield, Kansas. (From the College.)
- Southwestern Presbyterian University, Catalogue 1922. Clarksville, Tennessee. (From the University.)
- Spokane College, Catalogue 1921-22. Spokane, Washington. (From the College.)
- Spokane University, Catalogue 1921-22. Spokane, Washington. (From the University.)
- Spring Hill College, Catalogue 1922. Spring Hill, Alabama. (From the College.)
- State College of Washington, Catalogue 1922. Pullman, Washington. (From the College.)
- State University of New Mexico, Thirty-first Annual Catalogue 1921-22. Albuquerque, New Mexico. (From the University.)
- Stavers and Stavers, Booklet of Demag Electric Pulley Blocks. London, England, 1922. (From the Company.)
- Sterling College, Catalogue 1921-22. Sterling, Kansas. (From the College.)
- Sterling Varnish Company, Sterling Insulating Varnishes and Compounds Catalogue. Pittsburgh, Pennsylvania, 1922. (From the Company.)
- Stonega Coke and Coal Company, Catalogue of Coal and Coke. Big Stone Gap, Virginia, 1922. (From the Company.)
- Susquehanna University, Catalogue 1922-23. Selinsgrove, Pennsylvania. (From the University.)
- Swarthmore College, Catalogue 1922. Swarthmore, Pennsylvania. (From the College.)
- Sweet Briar College, Catalogue 1922-23. Sweet Briar, Virginia. (From the College.)
- Tarkio College, Catalogue 1921-22. Tarkio, Missouri. (From the College.)
- Taylor University, Catalogue 1921-22. Upland, Indiana. (From the University.)
- Tennessee State Mining Department, Annual Report for 1921 and Laws Governing and Regulating Mining in Tennessee. Nashville, Tennessee, 1922. (From the Department.)
- Thwing Instrument Company, Bulletin 11. Philadelphia, Pennsylvania, 1922. (From the Company.)
- Topping, Charles T., Machinery Company, Facts about Topping Pony-Ditchers. Pittsburgh, Pennsylvania, 1922. (From the Company.)



- Transylvania College, Catalogue 1921-22. Lexington, Kentucky. (From the College.)
- Trinity College, Catalogue for 1921-22 and 1922-23. Washington, District of Columbia. (From the College.)
- Tri-State College, Catalogue 1922-23. Angola, Indiana. (From the College.)
- Trumbull Electric Manufacturing Company, Bulletin No. 4. Plainville, Connecticut, 1922. (From the Company.)
- Truscon Steel Company, Truscon Foundry Flasks. Youngstown, Ohio, 1922. (From the Company.)
- Tufts College, Annual Catalogue 1922-23. Boston, Massachusetts. (From the College.)
- Tulane University of Louisiana, Catalogue 1922-23. New Orleans, Louisiana. (From the University.)
- Tusculum College, Catalogue 1921-22. Greeneville, Tennessee. (From the College.)
- Tyler and Company, Limited, Railway Signal and Permanent Way Engineer's Pocket Book. London, England, 1922. (From the Company.)
- Uehling Instrument Company, Bulletins 112 and 113. Paterson, New Jersey, 1922. (From the Company.)
- Union College, Catalogue 1922-23. Barbourville, Kentucky. (From the College.)
- Union College, Catalogue 1922-23. Schenectady, New York. (From the College.)
- United States Air Service, Information Circulars Nos. 360, 367, 370, 372, 373, and 374. Washington, District of Columbia, 1922. (From the Chief of Air Service.)
- United States Coast and Geodetic Survey, Annual Report of the Director for 1922. Washington, District of Columbia, 1922. (From the Director.)
- United States Department of Commerce, Financial Statistics of Cities Having a Population of Over 30,000, 1921. Washington, District of Columbia, 1922. (From the Department.)
- United States National Museum, Report on the Progress and Condition of the United States National Museum for the Year Ending June 30, 1922. Washington, District of Columbia. (From the Museum.)
- United States War Department, Report of the Chief of Engineers of U. S. Army, 1922, Parts I and II. Washington, District of Columbia, 1922. (From the Department.)
- Universitetets Mineralogiske Institut, Fifteen Publications issued during the years 1916-1922. Kristiania, Norway. (From the University.)
- University of Akron, Catalogue 1922. Akron, Ohio. (From the University.)
- University of Alabama, Catalogue 1921-22. University, Alabama. (From the University.)
- University of Buffalo, Catalogue 1921-22. Buffalo, New York. (From the University.)
- University of California, Catalogue 1922-23. Berkeley, California. (From the University.)
- University of Cincinnati, Catalogue 1921-22. Cincinnati, Ohio. (From the University.)



- University of Delaware, Annual Catalogue 1921-22. Newark, Delaware. (From the University.)
- University of Dubuque, Annual Catalogue 1921-22. Dubuque, Iowa. (From the University.)
- University of Georgia, Catalogue 1921-22. Athens, Georgia. (From the University.)
- University of Iowa, Catalogue 1921-22. Iowa City, Iowa. (From the University.)
- University of Kentucky, Catalogue 1921-22. Lexington, Kentucky. (From the University.)
- University of Leiden, Memorial Volume to Dr. Onnes. Leiden, Holland, 1922. (From the Secretary-Editor.)
- University of Maine, Catalogue 1922-23. Orono, Maine. (From the University.)
- University of Maryland, Catalogue 1922-23. College Park, Maryland. (From the University.)
- University of Missouri, Catalogue 1922. Columbia, Missouri. (From the University.)
- University of Montana, Bulletins 1, 2, 3 and 37. Missoula, Montana, 1919 and 1920. (From the University.)
- University of Nebraska, Catalogue 1921-22. Lincoln, Nebraska. (From the University.)
- University of Nevada, Catalogue 1922-23. Reno, Nevada. (From the University.)
- University of New Mexico, Bulletins Nos. 1 and 2 and Geological Series Nos. 3 and 4. Albuquerque, New Mexico, 1922. (From the University.)
- University of Notre Dame, Catalogue 1921-22. Notre Dame, Indiana. (From the University.)
- University of Omaha, Catalogue 1922-23. Omaha, Nebraska. (From the University.)
- University of Redlands, Catalogue 1922. Redlands, California. (From the University.)
- University of Richmond, Catalogue 1922. Richmond, Virginia. (From the University.)
- University of Santa Clara, Catalogue 1922-23. Santa Clara, California. (From the University.)
- University of the South, Catalogue 1921-22. Sewanee, Tennessee. (From the University.)
- University of South Carolina, Catalogue 1921-22. Columbia, South Carolina. (From the University.)
- University of South Dakota, Catalogue 1921-22. Vermilion, South Dakota. (From the University.)
- University of the State of New York, Annual Reports, Higher Education, vol. ii, and Secondary Education, vol. ii. Albany, New York, 1922. (From the University.)
- University of Tulsa, Catalogue 1921-22. Tulsa, Oklahoma. (From the University.)



- University of Utah, Bulletins 8, 9, 11, 12 and 13. Salt Lake City, Utah, 1916 to 1920. (From the University.)
- University of Wisconsin, Publications of the Washburn Observatory, vol. xiv, Part 1, Observations of Proper Motion Stars. Madison, Wisconsin, 1922. (From the University.)
- Upper Iowa University, Catalogue 1921-22. Fayette, Iowa. (From the University.)
- Ursinus College, Catalogue 1921-22. Collegeville, Pennsylvania. (From the College.)
- Valparaiso University, Catalogue 1922-23. Valparaiso, Indiana. (From the University.)
- Veeder Manufacturing Company, Catalogue of Veeder Counters. Hartford, Connecticut, 1922. (From the Company.)
- Vermont Department of Geology, Report of the State Geologist for 1919-1920. Burlington, Vermont, 1921. (From the State Geologist.)
- Virginia Bureau of Labor and Industrial Statistics, Twenty-fourth Annual Report. Richmond, Virginia, 1921. (From the Bureau.)
- Virginia Interment College, Catalogue 1922-23. Bristol, Virginia. (From the College.)
- Vitrefracx Company, The Irreducible Volume. Los Angeles, California, no date. (From the Company.)
- Wabash College, Catalogue 1922. Crawfordsville, Indiana. (From the College.)
- Washburn College, Catalogue 1921-22. Topeka, Kansas. (From the College.)
- Washington Department of Labor and Industries, First Report for Year Ending June 30, 1922. Olympia, Washington, 1922. (From the Department.)
- Washington Geological Survey, Bulletins 1-10, 12, 13, 16-23, 25 and 26 and Annual Report for 1902. Olympia, Washington. (From the State Geologist.)
- Washington and Jefferson College, Catalogue 1921-22. Washington, Pennsylvania. (From the College.)
- Washington Missionary College, Catalogue 1922-23. Takoma Park, Washington, District of Columbia. (From the College.)
- Washington University, Record for October, 1922. St. Louis, Missouri, 1922. (From the University.)
- Wellesley College, Catalogue 1922-23. Wellesley, Massachusetts. (From the College.)
- Wells College, Catalogue 1922-23. Aurora, New York. (From the College.)
- Wesley College, Catalogue 1922-23. Greenville, Texas. (From the College.)
- Wesleyan College of West Virginia, Catalogue 1922. Buckhannon, West Virginia. (From the College.)
- Wesleyan University, Catalogue 1922-23. Middletown, Connecticut. (From the University.)
- West Virginia Department of Mines, Annual Reports for 1919, 1920 and 1921. Charleston, West Virginia. (From the Department.)
- West Virginia University, Catalogue 1921-22. Morgantown, West Virginia. (From the University.)



- Westminster College, Catalogue 1922. Fulton, Missouri. (From the College.)
- Weston Electrical Instrument Company, Bulletin 2006. Newark, New Jersey, 1922. (From the Company.)
- Wheaton College, Catalogue 1921-22. Norton, Massachusetts. (From the College.)
- White, S. S., Dental Manufacturing Company, Flexible Shaft Driven Tools. New York City, New York, 1922. (From the Company.)
- Whitford, Noble E., History of the Barge Canal of New York State. Albany, New York, 1922. (From the Author.)
- Whiting Corporation, Catalogues Nos. 161 and 164. Harvey, Illinois, 1922. (From the Corporation.)
- Whitman College, Catalogue 1922. Walla Walla, Washington. (From the College.)
- Whittier College, Catalogue 1922-23. Whittier, California. (From the College.)
- Whitworth College, Catalogue 1922-23. Spokane, Washington. (From the College.)
- Willamette University, Catalogue 1922-23. Salem, Oregon. (From the University.)
- Williams College, Catalogue 1922. Williamstown, Massachusetts. (From the College.)
- Williamsport Wire Rope Company, Booklet of Wire Rope. Williamsport, Pennsylvania, no date. (From the Company.)
- Wittenberg College, Catalogue 1921-22. Springfield, Ohio. (From the College.)
- Woman's College of Alabama, Catalogue 1922. Montgomery, Alabama. (From the College.)
- Worcester Polytechnic Institute, Catalogue 1922-23. Worcester, Massachusetts. (From the Institute.)
- Wyoming Department of Geology, Bulletins 3A, 14, 15, 18, and Brief Reviews of the South Pass Gold District. Cheyenne, Wyoming, 1922. (From the State Geologist.)
- Wyoming State Department of Geology, Eleventh Biennial Report for October, 1920, to September, 1922. (From the Department.)
- Yankton College, Catalogue 1922. Yankton, South Dakota. (From the College.)

---

### BOOK NOTICES.

CAROTINOIDS AND RELATED PIGMENTS: THE CHROMOLIPOIDS. American Chemical Society, Monograph Series. By Leroy S. Palmer, Ph.D., Professor of Agricultural Bio-chemistry, University of Minnesota. 316 pages including indexes and bibliography, illustrations and plates, 8vo. New York, The Chemical Catalog Company. Price \$4.50 net.

With the formal statement that this book has the general merits of good printing, paper and illustrating that have characterized all the volumes so far issued in this A.C.S. series, the reviewer can pass to the interesting but somewhat difficult task of presenting the essential features thereof. A



difficult task, not because the subject is imperfectly handled, but because it takes the reader into a highly specialized field of bio-chemistry, a field which lies at present well outside the general scope of organic chemistry as presented in our standard text-books and taught in our colleges and schools.

Color is widely distributed in nature, and is by no means limited to living organisms. Many natural minerals are characteristically colored, and the chemist encounters a vast array of brilliantly colored products in inorganic work. "Color-tests" are now-a-days among the most common methods of analysis, and the enormous number of synthetic dyes that have been obtained from tar has had a profound influence on the course of events in the half century that has elapsed since the so-called "anilin colors" were commercially produced. Color, indeed, is the basis of beauty in nature. We may be impressed by the clouds and the seascape, but our reaction to a brilliantly colored scene is much more emotional. The old experiments of illuminating a variety of colored objects with monochromatic light, especially sodium light, will show us how tame would be the world around us if the production and perception of color did not exist.

Doctor Palmer points out that color arises from two distinct conditions, structure and actual power of absorbing certain rays of light. Structural origin is seen abundantly in the phenomena developed by reflection of light from colloidal particles or from the films, as in the soap-bubble. True pigments are substances that absorb certain colors when illuminated with white light and reflect the others. The reflected light determines the color of the active surface. In many cases, however, the separation is incomplete; much white light may be mixed with the reflected rays, and thus a misleading effect be produced. Gold, for instance, is red, but in a single reflection appears yellow; by repeated reflections the true color is obtained. In a considerable number of cases the separation results in one combination of waves passing through while the remaining waves are turned back. Such substances termed, "dichroic," give one color when looked at, and the complementary one when looked through. Many of the synthetic coal-tar colors show this property.

The book in hand is devoted to yellow, orange-yellow, orange-red and red pigments occurring in living organisms. The term "carotinoid" is derived from "carotin," the first yellow pigment isolated in crystalline form, occurring in the carrot, *Daucus carota* L. The name was used to include all plant chromolipoids, but investigation showed that differences exist between these, and the name was changed to carotins, many workers also using the term "carotin group." Carotin was found to be a hydrocarbon and the name "carotene" was proposed. Doctor Palmer states that the London Chemical Society favors the spelling "carrotene." What is the reason for this is not stated, and the name "London Chemical Society" is not quite apt, as the British organization has always been known as "The Chemical Society" without indication of country or special location.

In the progress of research, it was ascertained that some of these pigments are hydrocarbons and others contain oxygen. The former were distinguished by Zopf as "xycarotins," the others are "carotinins." These latter are capable of uniting with certain metallic elements. Another group of pigments is the



"xanthophylls." These, like the carotinoids, exist both in plants and animals and are related thereto.

The book leads into a field practically unknown to chemists engaged in teaching or in commercial work. Extensive as have been the researches and the bibliography thereof, many of the most frequently recurring names of investigators are unfamiliar in the general literature of the science. Yet the highly specialized nature of this line and the comparative lack of results directly bearing on the applied phase of the science, must not lead to any deprecation of the labor. The object of science is the discovery of truth; the benefit to be derived from knowledge is not the primary urge. In the book before us, indeed, a very interesting practical result is described. During the war, a strategic use was made of fake foliage. Canvass or other suitable material was painted to represent plants. It was found that real foliage reflects differently from ordinary green paint, and light filters were developed in the Eastman Laboratories by which the aviator was enabled to distinguish the true from the false, the latter appearing green and former red through these filters. Professor Wood in his researches in invisible light found that ordinary foliage photographed by infra-red light appears as if covered with snow.

From his viewpoint as a bio-chemist, Doctor Palmer is led to express opinions on the value of the carotinoids and allied substances in the life struggle of plants and animals. He is not at all favorable to the theories of mimicry and protective resemblance that have found such wide acceptance among naturalists since the days of Darwin and Wallace, and pays his respects to such views in anything but courteous phrase. Referring (p. 158) to a suggestion that a color in the eggs of an insect has been regarded as a protection, he says

"Although the writer is not in sympathy with the protective notions regarding animal colorations, believing that such phenomena are to be explained entirely on physiologic grounds, and not through theories built upon the assumption that colors impart the same sensations upon the retina of the eyes of lower animals that they do upon our own, it is nevertheless an interesting fact that insects apparently have the ability to impart derived pigments found in the blood to their eggs just as is found in the case of the higher oviparous animals."

Exception must be taken to the form, spirit and science of this sentence. The word "protective" should qualify "animal colorations," the theories deserve a kindlier allusion than to be called "notions," and the statement that the colors may be explained on physiologic grounds is a mere truism. All the phenomena in living organisms can be explained on physiologic grounds, using the term "physiology" to include the processes of physics, physical chemistry and chemistry, but the data at hand are too few to furnish such explanations. Doctor Palmer's criticism almost seems to involve the assumption that naturalists believe that the insect colors its eggs by intention, but the doctrine of natural selection is that a given living organism, having acquired by physiologic processes, without its conscious action or any outside consciousness some property or method which inures to its advantage in the struggle for



existence, this property or method will be likely to be perpetuated by inheritance and to be continuously advanced in relative function.

The allusion to the possibility that the lower animals do not have the same perceptions of color as human beings is little more than a red herring drawn across the trail. It is not a question whether an insect or a bird perceives a red mass upon a green leaf the same as we see them, but whether there is such a contrast as enables the animal to distinguish one object from the other.

High praise must be given to the author of the work for the patience and care with which the literature of this difficult subject has been searched and abstracted. The bibliography shows that his own labors have been extensive and fruitful. He has had in view not only a comprehensive presentation of the existing knowledge, but to indicate to beginners lines of investigation worthy of pursuit. In view, however, of the many lines of investigation now open, in which striking theoretical and practical results are likely to be obtained, it is doubtful whether the somewhat abstruse and certainly difficult field of the carotinoids and allies will be attractive to many. Doctor Palmer gives a scheme for the pronunciation of several of the most important terms used in the book. Exception may be taken to the accenting of "chromatogram" on the last syllable. That seems to make the pronunciation difficult and it is likely that most speakers will accent the antepenultimate. The tendency in English seems to be to move the accent towards the beginning of the word. "Par-e'-sis" has become "par'-e-sis," and "tel-e-graph'-y," "teleg'-raphy." Following the custom of most of the books issued by the publishing firm, some attempt is made at simplified spelling, but it is in a weak and practically useless form. The only noticeable change is in spelling sulphur and its derivatives with an "f," a change which involves no phonetic gain. It is a puzzle why xanthophyll and chlorophyll are not likewise spelled with "f" and further why a double "l" is used in these and similar terms. A far more useful modification would be to get rid of the final "e" in the names of binary compounds. A few typographic errors have been noted. These are all of the type practically unavoidable, and mostly not misleading. On page 42 in the last paragraph, "benzine" should be "benzene," on page 155 "*Insectia*" should be "*Insecta*" and on the same page and in the bibliography, page 287 "Medola" should be "Meldola."

An interesting question is whether there is any relation between carotin and vitamin A. This is discussed at considerable length. It has been declared by one investigator that the two are identical, but the data at hand negative that view. The decision is that although vitamin A like carotin and its allies is taken in by animals through food and not elaborated in the organism, the two are wholly distinct. In the course of the chapter, Doctor Palmer makes another criticism of the theories of mimicry and protective resemblance, telling us that he "does not possess a biologic viewpoint which is sufficiently developed along academic lines to appreciate 'function' as an abstract attribute of living organisms." *Tantæne animis caelestibus iræ?*

The reviewer's disagreement with some of the author's inferences as to the functions of plant and animal colors in interrelations in nature, that is,



in the struggle for existence, must not be allowed to obscure the commendation which the book deserves as a summary of the vast and intricate data already accumulated in this field, nor to belittle the author's own extensive contributions and his eminent fitness for the task he undertook. In passing from the pure science of the subject to accessory topics, he enters the stormy area of discussion of "design and purpose" in nature, in which difference of opinion is sure to arise and to be expressed with feeling. After all, perhaps, the world of science is benefited, as is the world of diplomacy, by an occasional dispute, and King Gama may be right when he sings:

"Oh, don't the days seem lank and long  
When all goes right and nothing goes wrong;  
And isn't life extremely flat  
With nothing at all to grumble at?"

HENRY LEFFMANN.

THE MICROSCOPY OF SMALL ARMS PRIMERS. By Emile Monnin Chamot. Heckscher Foundation for the Advancement of Research, Cornell University, Ithaca, New York, 1922. 61 pages, 21 plates, 2 figures in text, 23 x 30 cm.

A primer, or more precisely a percussion primer, is the tiny device, containing the priming composition and an anvil, which is placed in the bottom of a small-arms cartridge case for the purpose of initiating the ignition and consequent explosion of the powder charge enclosed in the case or shell. Percussion primers are the direct successors and most recent development of the percussion cap used on the nipples of the older forms of pistols and muskets. Like the percussion caps percussion primers each contain a minute quantity of a composition designed to promptly ignite and emit a spit of flame when struck a blow by the firing pin of the gun upon the anvil. Though the charge of the primer composition in the cup of a percussion primer may be but one-half of a grain or less in weight, yet unless the primer functions normally with certainty under all conditions of service use the whole system fails, rendering the firearm useless, and this effect is particularly disastrous in magazine rifles and machine guns, where the loading, firing and ejecting mechanism is operated by the explosion's gases, for a single defective primer in the whole train may interrupt the firing at a critical moment, put the gun out of action and turn the tide of battle. Moreover, certainty of action of primers became the more imperative when machine guns were so coördinated with the propellers of aircraft as to fire between the blades of the latter, since a hang-fire might result in the carrying-away of the blades of the propeller and the wrecking of the plane.

It was not surprising therefore that a feeling of the gravest apprehension spread through the nation when, shortly after the entrance of the United States into participation in the Great War, it was reported that the ammunition for the supply of our troops contained defective primers. Under House Resolution No. 134 of the Congress an investigation was carried out. The record of the testimony and opinions given at the "hearings" of the committee, published as a pamphlet of 178 pages, shows the reports to have been true and that misfires and hang-fires due to this cause were not inirequent. At once the War



Department sought experts in a variety of fields to bring their special knowledge and capacities to the remedying of these most serious defects. Among those thus called upon was Doctor Chamot, Professor of Chemical Microscopy in Cornell University and author of an authoritative manual in this field of science, who brought his special facilities, methods and technic to the solution of the problems of producing permanently reliable primers and of developing practical methods of inspection which would disclose defective primers and expose the nature of their defects so that they might be avoided in further manufacture. He found the subject of study so interesting that "After all work for the Ordnance Department ceased, the author continued the studies upon the material still in hand and upon such other primers and ammunition as he was fortunate enough to obtain. Not being now pressed for time, it was possible to check up doubtful facts and improve methods and apparatus. This monograph is based, therefore, almost entirely upon after-war data, and the illustrations, with three or four exceptions, are from photographs taken during this last period."

The topics covered in this monograph are the history and descriptions of early percussion caps and pin-fire cartridges; typical modern military rifle cartridges; the causes of primer malfunctions; manufacture of primers; microscopes for the investigation of primers; comparison microscopes; melting points determined microscopically; tools and appliances for microscopic primer studies; methods for removing primers from cartridges; microscopic examination of primer pellets; removing anvils from primers; wet primer pellets; texture of pellets; sectioning primers; microscopic appearance of pellets; microscopy of primer cups; protective coatings; microscopy of pellet components; firearm malfunctions; and the relative proportion of different types of malfunctions.

With the aid of an abundance of photographs and photomicrographs, Doctor Chamot describes in great detail the various instruments and tools (many of them devised for this research) employed in his investigations, as well as the technic he has developed so that hereafter primer manufacture may be properly supervised and consignments properly inspected. It has been generally believed that because primers are very sensitive to percussion they are equally sensitive to other mechanical effects. It was therefore a matter of much surprise to find they could be sectioned vertically so as to disclose the most important facts, their general morphology and internal structure relative to mis-fires, and very large numbers were thus sectioned in the author's laboratories with no disastrous results. In fact, following his technic and adopting his safeguards "*one may saw through the pellets of most primers with a fine-toothed saw almost as nonchalantly as through a piece of wood or metal.*" The many photomicrographs of sectioned percussion caps and primers shown are the most novel and interesting of the many illustrations presented in this brochure and they disclose to the least discerning a great variety of defects to which primers may be subject unless means are provided in advance for their prevention.

From an analysis of some hundred of cartridge mis-fires Doctor Chamot finds 28.5 per cent. due to defects in assembly and other mechanical imperfections, 25 per cent. to poorly compressed or thick pellets, 12.6 per cent. to too low a temperature of the "spit" of the primer, 7.7 per cent. to segregation



of the primer components and 12.59 per cent. to causes not enumerated. Other causes enumerated were incipient explosions, 4 per cent.; pellets too thin under the anvil, 4 per cent.; pellets which were probably cracked or were fired in the primer seating presses, 3.4 per cent.; pellets contaminated with oil, 2.2 per cent., and foreign matter under the anvils, 0.01 per cent., but seldom was primer malfunction due to a single imperfection only. One is impressed by this rehearsal of actual defects found with the extreme care that must be exercised in the manufacture of this tiny but fundamental and prime device. There seems to be something uncanny in the behavior of matter as when a larger particle of a comminuted component of the composition finds its way past the sieve it deliberately, apparently, seats itself over the anvil so as to receive the impact of the firing pin and, being by itself inert, prevents the initiation of the explosion, and yet this is well shown in Fig. 2 on p. 55, where an egg-shaped particle of potassium chlorate lodged in the manner described.

Little attention is given to the many specific formulæ for primer compositions, but the chemical and physical characteristics of the components of these mixtures are described in detail and the appearances of many of them as they are viewed under the microscope are shown in splendid photomicrographs so that the chemical and physical means for the identification of each of these components present in minute quantities in the field of the microscope is made very clear, but no reference is made to the potassium bromate that engaged attention at the hearings before Congress. Not the least ingenious of the methods presented is that for the determination of the melting points of small particles of these components, an instrument for this purpose having been devised for this investigation by providing an ordinary petrographic microscope with an electrically heated stage and a drawing camera so arranged that the observer can view the object being heated and the scale of the voltmeter at the same time.

This record adds many to the rapidly increasing list of examples from precise chemical investigations showing definitely the large effects of "little things" and the absolute necessity of taking full account of little things to secure a definite and uniformly reliable product. For instance, many "malfunctions" were examined in which distorted cups, due to unequal thickness, were the only defect which could be discovered. The shape and emplacement of an anvil and the curve of the primer pocket are contributing causes to success or failure. Even a feather edge on a cup may cause mis-fire. In testing by the "drop test" with a 4-ounce steel ball, the ball had to fall from 2 to 4 inches greater height to explode a primer having a feather-edged cup and a deep-seated anvil than was required to explode a normal primer. The tiny discs with which the pellets in the cups are covered to protect them from moisture, and which are therefore interposed between the pellet and the anvil, received attention. Frequently these discs are punched from very tough, long fibred, Manila paper, and sometimes this paper is coated with shellac. In some instances discs of foil made from tin-lead alloy are employed. Doctor Chamot found this paper to possess a low inflammability and to offer remarkable resistance to the explosion. "It therefore interposes a real barrier between the flash of the primer and the powder charge. It is



ruptured only with the greatest difficulty" and this is shown in one of the photomicrographs exhibited. Moreover "hard, stiff paper discs, such as result from too heavy shellacing, are apt to pucker and fold under the pressure of a decidedly conical anvil, and finally assume a funnel shape with a sharp point. This point is sufficiently hard and rigid to penetrate deeply into a fresh, soft pellet. One lot of primers prepared just as we entered the war was found to have most of the pellets so deeply indented by the paper that very little detonating mixture remained between anvil and cup. The point of the paper cone also probably deadened the blow of the striker and thus contributed in part to producing primers of poor quality and abnormally low sensitivity." He holds that "Whatever objections there may be to the use of thin metal foil (tin-lead alloy) it is certain that it properly protects the pellet, clings tightly to pellet and sides of the cup, and adequately water-proofs the primer, and is easily ruptured and completely destroyed by the explosion of the detonating mixture. Considerable care must, however, be taken in seating the discs."

Although the existence of the defects in primers rehearsed above, and others, were demonstrated, yet in reality a very large number of mis-fires which are blamed on primers are really due to arm or cartridge malfunctions. Moreover, "the non-standardization of firearms forces upon the manufacturers of primers a problem of the first magnitude. Primers are required which will properly function in all guns of the same calibre, irrespective of the spring tension of hammer or bolt, and irrespective of the size and the shape of the end of the firing pin." "It appears to be expected by ordnance men that a primer can be produced which will function equally as well in a gun delivering a firing-pin blow equivalent to a spring tension of about five pounds as in a gun delivering a twenty-five pound spring tension blow." To show that this charge of variations in blows and in the conformation of firing-pin points are facts photomicrographs of the heads of 35 primers of the same class, most of which had malfunctioned in machine guns or rifles, are presented, all the different .30 calibre machine-guns used in the American army being represented, and it is said "One who is familiar with the characteristics of the different guns will probably have little difficulty in assigning firing-pin marks each to its own proper gun. Besides a group—or type-characteristic—each individual arm usually imprints upon a primer a pattern peculiar to its own firing-pin. The microscope will almost unfailingly reveal whether a given number of primers have been fired in one or several different guns and will enable the investigator to decide which gun, if the guns are available for study." Doctor Chamot may not be aware that this last-mentioned method was resorted to, without success, in the endeavor to find the criminals in the notorious Brownsville riot.

This monograph is presented on heavy calendered paper throughout, which brings out the halftones in a vivid manner, and with clear-faced type. The Heckscher Foundation is to be congratulated in that one of its earliest publications should be so authoritative a document and presented in so attractive a form.

CHARLES E. MUNROE.



THE THEORY OF EMULSIONS AND EMULSIFICATION. By William Clayton, D.Sc., F.I.C. 160 pages, 22 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$3 net.

Technical terms are so extremely numerous in science that most persons shrink from searching into the primitive meaning even of those that have not been specifically coined. Yet there are curious instances of perversion of meaning by the course of events and by the laws of word evolution. Alcohol, for example, originally meant a fine powder, and in the early part of the nineteenth century, Davy spoke of the "alcohol of sulphur," meaning the finely divided precipitated form. So the word "emulsion" comes primarily from the Latin "emulgere," which means to drain out all liquid, especially to drain out milk. In one of its earliest uses it is spelled "emulsion." The term has long been applied to the intimate mixtures of two liquids not appreciably soluble in each other, and its use in this respect is derived from the physical nature of milk which is practically an emulsion of fat in a complex water solution. Considerable difference, however, exists between milk and the common emulsions. The liquid portion of normal milk probably contains proteins in a colloidal condition, in which the milk globules float. The latter are due to the fatty degeneration of the epithelial cells lining the tubules of the milk gland, so that in a certain sense the secretion is a process of disease. Milk globules do not spontaneously coalesce, which property may be due either to a distinct membrane or to a hardened external layer. The most familiar forms of emulsions are those of oil, either fatty or hydrocarbon, in water. Some of them have been long known and the methods of obtaining them invented in a remote past. The scientific study of the conditions dates from a recent period and is one of the phases of rapid development of colloid chemistry.

Doctor Clayton has collected in this book a very large amount of data bearing upon this subject which has both practical and theoretical interest. An emulsion is scientifically defined as a system containing two liquid phases one of which is dispersed as globules in the other. The earliest types of emulsions were those of oily, that is, water-repellent liquids dispersed in water. Temporary emulsions of this type can be easily obtained by shaking the oil and water together, but the globules soon begin to coalesce and two strata are formed. Water-in-oil is a more recent type. When the proportion of oil to water is very small, a stable emulsion may be obtained by mechanical means, such an effect being often observed in engine-condenser water, the proportion of oil being about 1 in 10,000. Here the physical condition approaches that known as colloidal. For preparing stable emulsions with appreciable proportions of both ingredients, a third substance is usually required. Obviously, the nature of the emulsifying agent materially affects the emulsion produced. Water-soluble colloids promote the formation of oil-in-water forms and oil-soluble colloids promote the reverse conditions. Pharmaceutic emulsions have long been extensively used, principally the oil-in-water form and a number of substances have been employed as determinants. Alkalies act merely by forming soaps with the free fatty acids present in the oils, soaps being excellent emulsifiers.

In addition to presenting the physics and chemistry of emulsification and the discussion of the theories now or formerly held concerning the phenomena,



an interesting chapter is added on de-emulsification. This has become of great industrial importance on account of the occurrence of natural emulsions of valuable liquids, and the frequent production of tenacious forms in some manufacturing operations. Oil wells not infrequently yield a product containing considerable closely intermixed water. The majority of this settles out on standing, but a small proportion remains. As crude oil, to be saleable, must not contain more than 2 per cent. of water many processes have been devised to get rid of the excess. It is believed that the emulsifying agent in these cases is asphalt. Doctor Clayton divides the procedures for removing water into three classes: Electrical, chemical, and mechanical. The electrical method depends principally upon the tendency of the water globules to follow the passage of an electric current. Cottrell, whose methods of dealing with dusts are well known, was the pioneer in patents for such de-emulsification. A plate is given of very large dehydrating plant in California dealing with a very troublesome emulsion of 40 per cent. of water. In connection with the discussion of the electrical methods, a striking illustration of the progress of the action is given by means of the reproduction of a motion picture taken by magnification and showing the gradual coalescing of the oil globules. A mixture consisting principally of sodium oleate is marketed for this purpose. Many other chemical methods are mentioned. Centrifugal separation has long been employed in the removal of butter-fat from milk. The DeLaval separator, though not the first machine devised for the purpose was the first one operating continuously, and is widely known. The principle of the centrifuge has been applied in many ways, and very high-speed forms have been recently introduced.

High commendation must be given to the author of this work, not only for the thoroughness with which the field has been garnered, but to the excellent form in which the material has been presented. One most commendable feature is the manner in which references are given. These are very numerous. Journal articles are quoted both by year and volume and the latter is printed in heavy-faced Arabic numerals thus avoiding the complex Roman numbers. In quoting books the year of publication is given. The mechanical execution of the book is also highly commendable and the work may well serve as a model for monographs of its kind.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 136, Damping Coefficients Due to Tail Surfaces in Aircraft, by Lynn Chu, Massachusetts Institute of Technology, Condensed and Modified by Edward P. Warner. 14 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

The object of the investigation described in this report was to compare the damping coefficient of an airfoil as calculated from a knowledge of the static characteristics of the section with those obtained experimentally with an oscillation. The damping coefficients so obtained, according to the conventional notation, can be considered either as due to pitching or as due to yawing, the oscillation in these experiments being so arranged that the surfaces oscillate about a vertical axis. This is in reality the case when the influence



is yawing about the standard Z-axis, but it can also be considered as a pitching motion when the model is so rigged that its standard Y-axis becomes vertical. This horizontal oscillation has the advantage of eliminating the gravity action and avoiding the use of counterweights, whose presence in the wind-tunnel is undesirable because of their interference with the air flow. The real point of the investigation was to separate the damping due to rotation from that due to translation. By varying the distance between the centre of pressure and the centre of rotation on the oscillator, the variation of damping moment can be observed and the rotational and translational effects can be separated.

Report No. 143, *Analysis of Stresses in German Airplanes*, by Wilhelm Hoff, Director of the Deutsche Versuchsanstalt für Luftfahrt. 52 pages, illustrations, plates, diagrams, quarto. Washington, Government Printing Office, 1922.

This report contains an account of the origin of the views and fundamental principles underlying the construction of German airplanes during the war. The report contains a detailed discussion of the aerodynamic principles and their use in determining the strength of airplanes, the analysis of the strength qualities of materials and in the construction, the calculated strength of air flows and a description of tests made in determining the strength of airplanes.

Report No. 145, *Internal Stresses in Laminated Construction*, by A. L. Heim, A. C. Knauss and Louis Scutter. Forest Products Laboratory. 56 pages, illustrations, quarto. Washington, Government Printing Office, 1922. Price 10 cents.

This report reviews the procedure employed in an investigation of the sources and influence of internal stresses in laminated construction, and discusses the influence of shrinkage and swelling stresses caused by atmospheric conditions upon the tensile strength across grain in laminated construction with special reference to airplane propellers.

The investigation covered three sources of internal stress, namely, the combination of plain-sawed and quarter-sawed material in the same construction, the gluing together of laminations of different moisture contents, and the gluing together of laminations of different densities.

Glued specimens and free specimens, made up under various manufacturing conditions, were subjected to various climatic changes inducing internal stresses and then were tested. The strength of free unstressed pieces served as a standard of comparison for glued pieces and indicated what internal stresses were developed in the glued construction.

Report No. 151, *General Biplane Theory*, by Max M. Munk. 47 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

Report No. 151 deals with the air forces on a biplane cellule. The first part of the report deals with a two-dimensional problem neglecting viscosity. For the first time a method is employed which takes the properties of the wing section into consideration. The variation of the section, chord, gap, stagger, and decalage are investigated, a great number of examples are calculated, and all numerical results are given in tables. For the biplane without stagger is found that the loss of lift in consequence of the mutual influence of the two wing sections is only half as much if the lift is produced by the curva-



ture of the section as it is when the lift is produced by the inclination of the chord to the direction of motion.

The second part deals with the influence of the lateral dimensions. This has been treated in former papers of the author, but the investigation of the staggered biplane is new. It is found that the loss of lift due to induction is almost unchanged, whether the biplane is staggered or not.

The third part is intended for practical use and can be read without knowledge of the first and second parts. The conclusions from the previous investigations are drawn, viscosity and experimental experience are brought in, and the method is simplified for practical application. Simple formulas give the drag, lift, and moment. In order to make the use of the simple formulas still more convenient, tables for the dynamical pressure, induced drag, and angle of attack are added so that practically no computation is needed for the application of the results.

Report No. 152, *The Aerodynamic Properties of Thick Aerofoils*, by F. H. Norton and D. L. Bacon. Langley Memorial Aeronautical Laboratory. 15 pages, diagrams, quarto. Washington, Government Printing Office, 1922. Price 5 cents.

This investigation was undertaken for the purpose of studying the effect of various modifications in a given wing section, including changes in thickness, height of lower camber, taper in thickness, and taper in plan form with special reference to the development of thick, efficient airfoils. The method consisted in testing the wings in the N.A.C.A. 5-foot wind-tunnel at speeds up to 50 metres (164 feet) per second while they were being supported on a new type of wire balance. Some of the airfoils developed showed results of great promise. For example, one wing (No. 81) with a thickness in the centre of 4.5 times that of the U.S.A. 16 showed both a uniformly higher efficiency and a higher maximum lift than this excellent section. These thick sections will be especially useful on airplanes with cantilever construction.

Report No. 153, *Controllability and Manœuvrability of Airplanes*, by F. H. Norton and W. G. Brown. Langley Memorial Aeronautical Laboratory. 18 pages, illustrations, quarto. Washington, Government Printing Office, 1922. Price 5 cents.

In this report are given the results of investigations carried out for the purpose of studying the behavior of the JN4h airplane in free flight under the action of its controls and from this to arrive at satisfactory definitions and coefficients for controllability and manœuvrability. The method consisted in recording the angular velocity about the three axes, together with the airspeed, control positions, and acceleration. An analysis of the records leads to the following results:

1. Both the maximum angular velocity and maximum angular acceleration are proportional to the displacement of the controls.
2. Both the maximum angular velocity and maximum angular acceleration for a given control movement increase with the airspeed, rapidly immediately above the stalling speed, then nearly proportional to the speed.
3. The time required to reach each maximum angular velocity is constant for all airspeeds and control displacements for a given airplane.



4. The minimum time required to reverse the direction of an airplane by a steeply banked turn is a rough indication of its general manœuvrability.

5. Doubling the lateral moment of inertia of an airplane increases the time required to bank at  $90^\circ$ , with a maximum control angle, by only 10 per cent.

6. Controllability has been defined as applying to the moment produced about the centre of gravity by the action of the controls and manœuvrability as the resultant motion.

7. A simple method is described for measuring the controllability coefficients  $\frac{dL}{di_x}$ ,  $\frac{dM}{di_y}$ , and  $\frac{dN}{di_z}$ , and the manœuvrability coefficients  $l_\phi$ ,  $l_\epsilon$ ,  $l_\psi$ , and  $\frac{(V_{min})^2}{g}$ .

These results are of practical value, as they give a quantitative means of measuring airplane manœuvrability and controllability, which will allow designers to accurately compare the merits of different airplanes.

Report No. 155. *A Study of Airplane Manœuvres with Special Reference to Angular Velocities*, by H. J. E. Reid. Langley Memorial Aeronautical Laboratory. 9 pages, illustrations, quarto. Washington, Government Printing Office, 1922. Price 5 cents.

With a view to increasing our knowledge on the behavior of the airplane during various manœuvres and to obtain values of the maximum angular velocities and accelerations in flight, this investigation was undertaken.

The method consisted in flying a JN4h airplane through various manœuvres while records were being taken of the control position, the airspeed, the angular velocity and the acceleration along the Z-axis. The results showed that the maximum angular velocity about the X-axis occurred in a spin and amounted to 2.43 radians per second, while about the Y-axis the maximum was 0.96 radian per second in a barrel roll. The maximum angular acceleration about the X-axis of  $-2.10$  radians per (second)<sup>2</sup> occurred in a spin, while the maximum about the Y-axis was 1.40 radians per (second)<sup>2</sup> when pulling out of a dive. These results have direct application to the design of airplane parts, such as propeller shaft and instruments.

Report No. 156. *The Altitude Effect on Air Speed Indicators—II*, by H. N. Eaton and W. A. McNair. 46 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

The report opens with a discussion of the theory of the performance of airspeed nozzles and of the calibration of the indicators, from which the theory of the altitude correction is developed. Then follows the determination of the performance characteristics of the nozzles and the calibration constants used for the indicators. In the latter half of the report the viscosity correction is computed for the Zahm Pitot-Venturi nozzles, army and navy types, which are the most commonly used airspeed nozzles in the United States. It will be found that the viscosity correction is far from negligible, since under certain conditions it may amount to 20 per cent. or more of the indicated airspeed. Tables and plots are given to enable the readings of Pitot type and Zahm Pitot-Venturi type indicators to be corrected for any atmospheric conditions which may be experienced by either heavier-than-air or lighter-than-air craft and for airspeeds up to approximately 200 miles per hour. Evidence is also adduced tending to show that the effect of the compressibility of the



atmosphere on the performance of Venturi airspeed nozzles is not numerically greater than the corresponding effect on Pitot tubes, and can be neglected over the range of flying speeds commonly attained to-day.

UNITED STATES COAST AND GEODETIC SURVEY, TERRESTRIAL MAGNETISM. Magnetic Declination in the United States for January 1, 1920, by Daniel L. Hazard, Assistant Chief, Division of Terrestrial Magnetism. 30 pages, map. 8vo. Washington, Government Printing Office, 1922. Price, five cents.

This publication is intended primarily to supply information regarding the earth's magnetism needed by navigators and land surveyors, but the data which it contains are of much value also to map makers and geophysicists.

The magnetic work of the United States Coast and Geodetic Survey, begun as one of the essential parts of the preparation of nautical charts of the coastal waters, has been extended to cover the interior of the country to meet the needs of the surveyor. Nearly all of the early land surveys in the United States were made by compass and the boundaries in the deeds were defined by compass bearings, and in many localities and for certain kinds of surveying (especially the retracing of the lines of old compass surveys) the compass is still in use. The compass does not, in general, point true north nor is its direction at any place constant, hence knowledge of the compass variation (magnetic declination) and its changes is required by those who make use of the compass. The object of this publication is to supply that information for the United States. The distribution of the magnetic declination and its annual rate of change for the beginning of 1920 are shown graphically on an isogonic chart. The secular change of the declination since 1750, or the date of the earliest observations, is given in tabular form for one or more places in each State. Tables are given also to show the manner in which the declination changes in the course of the day, the so-called diurnal variation.

Methods of determining the true meridian are explained, so that the surveyor may determine the magnetic declination for himself at places where there is no meridian line or other true bearings available.

OUTLINES OF THEORETICAL CHEMISTRY. By Frederick H. Getman, Ph.D. Third edition, thoroughly revised and enlarged, xi-625 pages, 149 illustrations, 8vo. New York, John Wiley and Sons, Incorporated, 1922. Price \$3.75.

The "small thin volume" of the first edition of Remsen's "Theoretical Chemistry" was at one time the American student's principal guide to the fundamentals of the science. In the earlier treatises on this subject, mathematics had but little concern. Chemical formulæ have to the uninitiated the appearance of algebra, but have no appreciable relation to it. A wise change was made when chemists began to write the exponents as inferiors, a change which, unfortunately, our French co-workers have not yet adopted. Most of them, however, have got over using Az for N.

The development of physical chemistry, and the invasion of physical concepts and physical methods into chemical procedures have greatly changed



the aspects of our works on the theories of the science. Data of all kinds have accumulated and great shifting has taken place in the views as to many forms of chemical reactions. The first edition of Remsen issued 1877 was a 12mo of 228 pages. A hasty inspection of its pages does not show one algebraic formula. The book before us, an octavo of over six hundred pages, bristles with complex expressions involving higher mathematics. Being a third edition, it is not necessary for the reviewer to discuss in any detail its merits. The first edition was published in 1913. The table of contents shows that the subject is fully covered. The last chapter gives twenty-four pages to a lucid and comprehensive exposition of the latest views on atomic structure, in the course of which isotopy is noted, and this subject is also included in the section on the electrical theory of matter. In this connection attention may be called to an unhappy development in nomenclature. Dr. A. W. Stewart in 1918, in an article in the *Philosophical Magazine*, suggested the word "isobare," in application to elements having the same atomic weight, but differing in properties, a sort of converse of "isotope." He remarks that the word "isobar" would be preferable but this has already been appropriated in meteorology as the term for the lines of equal barometric pressure, in comparison with "isotherm." To prevent this overlapping, Stewart changed the spelling slightly. It is to be regretted that he did not at the same time either indicate the pronunciation or adopt such a spelling as will leave no serious doubt in that line. It is now uncertain whether the last syllable rhymes with "far" or with "fare." Analogy is no definite guide in English, but it is to be hoped that the value of the final, but silent, "e" will be preserved, and that the term will rhyme with "fare," awkward as that is considering the etymology. Such pronunciation will, however, have the advantage of following the analogy of "isotope."

As regards the book itself, it is an excellent guide to the subject, well printed on good paper.

HENRY LEFFMANN.

DIE TECHNIC DER ELEKTRISCHEN MESSGERÄTE. By George Keinath, Eng. D. Second enlarged edition, vii-477 pages, 400 illustrations in the text. Munich and Berlin, R. Oldenbourg, 1922. Price, paper, \$4.80; bound, \$5.

A comprehensive review of the first edition of this work was published in this JOURNAL for December, 1921. The fact that a second edition has been called for in so brief a period is the best evidence of the merit of the book and of the place that it fills. Though enlarged, the thickness of the book is less than in the case of the first edition, by the use of a thinner but good quality paper. The text is not materially changed from the first edition and what was said of that will apply to the present work. The section on temperature measurement has been omitted in this edition, as the author intends to treat this subject in a separate work under the title "Die Technik der elektrischen Pyrometrie." Important advances that have occurred in the interval between the two editions have been included. Certain rules formed by the Association of German Electricians have been added as an appendix.

HENRY LEFFMANN.



SPACE-TIME-MATTER. By Hermann Weyl. Translated by Henry L. Brose. 324 pages and index, 8vo. New York, E. P. Dutton and Company, 1922.

This book has grown out of a series of lectures delivered at the Zurich Polytechnikum in the summer term of 1917. Its subject is Einstein's Theory of Relativity, that theory which "has advanced our ideas of the structure of the cosmos a step further. It is as if a wall which separated us from Truth has collapsed. Wider expanses and greater depths are now exposed to the searching eyes of knowledge, regions of which we had not even a presentiment. It has brought us much nearer to grasping the plan that underlies all physical happening." The author desired "to present this great subject as an intermingling of philosophical, mathematical, and physical thought, a study which is dear to my heart," but he is constrained to admit that "the mathematician predominates at the expense of the philosopher." The reader, for whom signs of integration and summation, hexaspherical coördinates and vector analysis have no terrors, will find here an interesting and logical development of the theory. From a differential equation he will be led to draw the conclusion that "space is closed and hence finite." He will come to understand why light rays act as if attracted by the sun and, again, what is the basis for holding that a line in the spectrum of sunlight should lie a little nearer to the red than the same line produced upon the earth. In spite of his previous conviction that the force of gravitation is instantaneously propagated he will be compelled to grant that "every change in the distribution of matter produces a gravitational effect which is propagated in space with the velocity of light."

The non-mathematical reader must not infer that this admirable book is of no value for him. On the contrary he will find much of the highest interest. There is, for example, the discussion of non-Euclidean geometry from Proclus onward, but he will in general need to rest content with the conclusions of the mathematical arguments.

To every one who has not assimilated this disturbing theory it will come as something of a shock to read "We are to discard our belief in the objective reality of simultaneity; it was the great achievement of Einstein in the field of the theory of knowledge that he banished this dogma from our minds, and this is what leads us to rank his name with that of Copernicus." He will be reassured by this "However great is the revolution produced in our ideas of space and time by Einstein's theory of gravitation, the actual deviations from the old theory are exceedingly small in our field of observation. Those which are measureable have been confirmed up to now. The chief support of the theory is to be found less in that lent by observation hitherto than in its inherent logical consistency, in which it far transcends that of classical mechanics, and also in the fact that it solves the perplexing problem of gravitation and of the relativity of motion at one stroke in a manner highly satisfying to our reason."

A valuable bibliography, six pages in length, is given. The volume, as is proper, closes with an index. The fundamental character of the discussion is indicated by the appearance of the terms "earlier and later" and "later" in the list of subjects. We miss any reference to Levi-Civita in the index and, as a reviewer should find at least one error, let it be noted that the reference



to the heat developed according to Joule's Law is to be found, not on page 162, but on the next page.

The translator has rendered the book into good English that rarely, if indeed ever, carries with it the flavor of a translation.

GEORGE F. STRADLING.

ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA, CHEMICAL, PHYSICAL AND TECHNOLOGICAL. Published under the patronage of the International Council of Research and the International Union of Pure and Applied Chemistry. With numerous collaborators. Volume iv, parts 1 and 2, 1375 pages, 4to. Paris, Gauthier-Villars et Cie., 1921; American distributors, University of Chicago Press.

This enormous collection of data, from the wide fields of chemistry, physics and technology, is a welcome addition to the literature of the science. It represents great labor and care and it is fortunate that the material has been presented in such excellent form and so conveniently classified. The main text is in French but the running heads, which give information as to the special subjects on each page, are in French, German, English and Italian. The use of French probably is the best expedient. German is much too complicated for an international language and Italian is just beginning to make its impression on purely technical literature. It has indeed been prominent in other fields for centuries. It is gratifying to note that French editors have been willing to abandon the eccentricity of writing chemical formulas with the exponents as superiors, which they have so long been doing. The chemical formulas in this work are written as they are in the works of the rest of the world. French chemists gave up some years ago the practise of writing Az for N, but they have held on with persistence worthy of a better cause to the old method of writing atomic numbers.

It is not possible to subject this publication to criticism as would be done with a text-book on science. Its value depends entirely upon the thoroughness of the selection and the care which has been taken to reproduce the data, as found in the numerous authorities quoted. A commendable feature is that, with references, the year as well as the volume is given and the volume is printed in full-faced Arabic type, instead of the Roman letters that are still unfortunately the custom among many scientists, especially those under the spell of British conservatism. It is to be hoped that a volume like this which has such wide uses will be a missionary agent in the reform in bibliographics. Series (if any), year, volume (in full-faced Arabic type) and page; this is the order that should be observed. It is not necessary to put the year in parenthesis, but the series numbers should be in brackets, and, of course, lead off the quotation. An incidental advantage of this volume is that it gives the official equivalents in the four languages of an immense number of technical terms. Students who are acquiring a knowledge of other tongues than their own, will be greatly aided by these data, since, though not so intended, it is a "tetraglot" dictionary. The mechanical execution of the book is good; the type is of the face that is common in French works, not quite so vivid as some of the faces used in English books, but still quite clear. The paper and printing



are commendable. The book takes rank at once among the most valuable reference works of the worker in the physical sciences.

HENRY LEFFMANN.

**BELT CONVEYORS AND BELT ELEVATORS.** By Frederic V. Hetzel, M.E., Member of A.S.M.E. and The Franklin Institute. New York, John Wiley and Sons, Inc.; London, Chapman and Hall, Ltd. Cloth, 6 x 9 in., 333 pages; half-tones and line cuts. Price, \$5 (25s net).

The mechanical handling of materials which lessens human labor is a subject of universal interest but its possibilities and applications are especially the concern of factory managers and production engineers who have handling problems to solve or transportation costs to reduce. The diversified lines of handling machinery now offered, new applications of handling methods constantly introduced and improved types of handling facilities manufactured, make it incumbent upon designing and operating engineers to keep posted on the latest developments in the handling and transportation fields.

Much of the literature published on this subject is too general or too limited in scope, largely descriptive and often fails to include general principles, economic considerations, or the basic data needed. A commendable contribution to recent technical literature, which is exceptionally thorough in its treatment of its subject, is "Belt Conveyors and Belt Elevators."

As chief engineer for thirteen years after a previous service as chief draughtsman for Link Belt Company, Mr. Hetzel was responsible for the design of many varieties of elevating and conveying machinery and acquired a wide experience and thorough knowledge of material handling equipment.

His new book is a thorough and practical treatise and presents for the general use of engineers and manufacturers specialized information, useful data and working formulæ which are not included or conveniently presented in trade catalogues and not widely known outside of the material-handling field. The book covers recent developments in both American and European practice. The information is impartially presented with no "axe to grind" and points out the merits of equipment for a particular service without attempting to boost the product of any favorite manufacturer.

The principles and reasons underlying the design, applications and service of belt conveyors and belt elevators for different classes of materials are fully discussed. The book is well illustrated with detail drawings, photographic views and charted curves. Tables of sizes, capacities, power consumption and other useful data are present in convenient form for engineers or manufacturers who have handling problems to solve. The text is concisely written, with frequent cross-references as well as mention of other sources of information. The book is a worthy and useful contribution to material handling literature.

HAROLD T. MOORE.

**THE MICROSCOPICAL EXAMINATION OF FOODS AND DRUGS.** By Henry Greenish, F.I.C., F.L.S. Third edition, xx-379 pages, index and 209 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1922. Price, \$4.50 net.

This is a compact volume covering all the important data relating to the examination of commercial drugs and foodstuffs, as far as the microscope is



employed in such work. The many illustrations will give the student and analyst vivid ideas of the appearance of the substances. All the illustrations are drawings, but they have been carefully made, and, while necessarily somewhat schematic, are satisfactory. Brief directions are given for the preparation of specimens for the microscope, and an appendix gives a list of solutions commonly employed. It is to be noted that the spelling "gramme" is employed, and the persistence with which the British hold on to this unnecessary method is discouraging to those who would like to simplify English spelling. However, recent works on chemistry that have emanated from British presses have shown a slight reforming tendency, and we may hope that in time the spelling "gram" will be usual. Those already fairly familiar with the technic of the microscope will find the work useful in detecting adulterations and determining the nature of powdered vegetable substances. The book is clearly printed on paper of moderate quality and its compactness makes it especially suitable for the student.

HENRY LEFFMANN.

HANDBOOK OF THE CENTRAL HIGH SCHOOL OF PHILADELPHIA. 132 pages, 17 illustrations, 8vo. Philadelphia, The Barnwell Foundation, 1922.

This book has been prepared and printed for distribution among the students and graduates of the Central High School by the Mary Gaston Barnwell Foundation, established under the Will of James Gaston Barnwell, A.M., a member of the sixteenth class, which graduated from the school in July, 1850. In his Will he wrote:

"Whatever reputation and success I have attained, however moderate, being the result, under Providence, of two causes, first, the training of a good mother who always inculcated and practiced the highest principles of honor and especially of moral courage regardless of immediate or apparent results, and secondly, to the education which I received in the Public Schools of Philadelphia and especially in the Central High School, I wish to honor the memory of that mother by practically encouraging and rewarding the practice of the same high principles by the Students and Graduates of the School."

While the handbook is primarily for the Central High School student and alumnus, yet it contains much information of general interest, for this institution, since its founding, has been in fact, as it should be in name, the city college, and, since 1849, has possessed the full powers of a university by Act of Assembly. Lists of notable teachers of the past and of representative alumni of every class contain the names of many men who have attained eminence in the various fields of science, and include many members of The Franklin Institute. The first president of the school was Alexander Dallas Bache, the great-grandson of Benjamin Franklin. The astronomical observatory was the fourth to be established in the United States. The inventions of Edwin J. Houston and Elihu Thomson in the field of electricity were developed in the laboratories of the school.

In the pages devoted to student organizations, reference is made to the work of The Natural History Society, The Chemistry Club, The Radio Club, The Camera Club, The Astronomical Society, and The Geographical Society, showing that the deep interest in things scientific still pervades the student body.

JOSEPH S. HEPBURN.



## PUBLICATIONS RECEIVED.

*The Theory of Emulsions and Emulsification.* By William Clayton, D.Sc. 160 pages, illustrations, plates, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$3.

*Industrial Organic Chemistry*, adapted for the use of manufacturers, chemists, and all interested in the utilization of organic materials in the industrial arts. By Samuel P. Sadtler, Ph.D., LL.D., and Louis J. Matos, Ph.D. Fifth edition (revised, enlarged, and in part rewritten). 691 pages, illustrations, plates, 8vo. Philadelphia, J. B. Lippincott Company, 1923. Price, \$8.

*Plastics and Molded Electrical Insulation.* By Emile Hemming. 313 pages, illustrations, plates, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price, \$5.

*Practical Physiological Chemistry.* A book designed for use in courses in practical physiological chemistry in schools of medicine and of science. By Philip B. Hawk, M.S., Ph.D. Eighth edition, revised. 693 pages, illustrations, colored plate, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$5.

*The Quantum Theory.* By Fritz Reiche, Professor of Physics in the University of Breslau. Translated by H. S. Hatfield, B.Sc., Ph.D., and Henry L. Brose, M.A. 183 pages, illustrations, 12mo. New York, E. P. Dutton and Company, no date. Price, \$2.50.

*Institut International de Physique Solvay.* Atomes et Électrons. Rapports et discussions de Conseil de Physique tenu a Bruxelles du 1er au 6 Avril, 1921. Publiés par la Commission administrative de l'Institut et MM. les Secrétaires du Conseil. 271 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 20 Francs.

*Tables Annuelles de Constantes et Données Numeriques de Chimie, de Physique, et de Technologie*, publiee sous le patronage de l'Union de Chimie pure et appliquée par le Comité international nommé par le VII<sup>e</sup> Congrès de Chimie appliquée. Volume iv, Années 1913, 1914, 1915, 1916. Two volumes, quarto. Paris, Gauthier-Villars et Cie.; Chicago, University of Chicago Press, 1921.

*U. S. Bureau of Mines:* Bulletin 202, Electric Brass Furnace Practice, by H. W. Gillett and E. L. Mack. 334 pages, illustrations, plates, 8vo. Bulletin 218, The Technology of Slate, by Oliver Bowles. 132 pages, illustrations, plates, 8vo. Technical Paper 287, Preparation of Light Aluminum-Copper Casting Alloys, by R. J. Anderson. 44 pages, plates, 8vo. Washington, Government Printing Office, 1922.

*National Advisory Committee for Aeronautics:* Technical Notes No. 124, Downwash of Airplane Wings, by Max Munk and Gunther Cario. 9 pages, diagrams, quarto. No. 125, Results of Experimental Flights at High Altitudes with Daimler, Benz, and Maybach Engines to Determine Mixture Formation and Heat Utilization of Fuel, by K. Kutzbach. 11 pages, diagrams, quarto. No. 126, Absolute Dimensions of Karman Vortex Motion, by Werner Heisenberg. 10 pages, diagrams, quarto. Washington, Committee, 1923.



## CURRENT TOPICS.

**Liquid Oxygen in Warfare.** SIR JAMES DEWAR. (Royal Institution of Great Britain, 1919.)—The members of the Royal Institution of Great Britain were engaged in research work for the British Government during the late war and one of the lines in which investigation was extensively carried on was the use of liquid oxygen. Professor Dewar, being especially qualified by extended researches, was directly engaged in this line and on January 17, 1919, presented a communication at the Weekly Evening Meeting of the Institution, giving an account of some of the more novel and important applications made.

The liquefaction of oxygen in the laboratories of the Royal Institution in 1884 was followed by the introduction of commercial methods for obtaining liquid air from which oxygen was subsequently obtained. The manufacture reached the amount of about one hundred twenty tons of liquid air per day, more than half of which was used in the oxy-acetylene blowpipe for cutting armor plates and welding. This work was carried out largely by the British Oxygen Company.

In this process a large amount of nitrogen was obtained which was practically useless, but very soon processes for its fixation in the form of important compounds were devised. The German dye industry spent large sums for securing water-power in Sweden in order to use the electric methods of fixation. These industries, however, pursued the problem along a much different line and finally developed, under the guidance of Haber, the now well-known process of direct union of nitrogen with hydrogen under very high pressure by the aid of a catalyst. Very large plants were erected in Germany for this purpose and it is probable that if such methods had not been well developed, Germany would have been unable to obtain the chemicals necessary for the manufacture of high explosives in the amount needed in the war. The Haber process yields ammonia directly which may be converted easily into nitric acid.

The lecture proceeded to describe the general characteristics of liquid oxygen. In the spectroscope three well-defined bands are seen in the orange and green. It is highly magnetic and shows very strikingly the spheroidal state. The use for explosive purposes which has now become of considerable importance is easily illustrated by soaking some cotton in liquid air and applying a light. The mass burns with a brilliant flash like gun-cotton. Finely divided organic matter mixed with liquid oxygen can be used for blasting when packed into a rock boring and detonated by an electric discharge. It has the advantage of retaining its explosive properties only



for a short time with consequent absence of danger from any unexploded charge.

An important war-time application of liquid oxygen was to supply oxygen gas for airmen at high altitudes and also for treatment of "gassed" cases in trench or hospital. For this purpose the liquid was volatilized from some form of vacuum container by regulated influx of heat, whence the gas was conveyed by tubes to mouth-pieces for breathing. Apparatus of this kind was found in German aeroplanes brought down when raiding London. This method has the advantage over that of carrying the necessary oxygen compressed in steel cylinders, in that it is much lighter to carry, and less cumbersome.

Three methods were devised for this purpose: Syphon evaporation, electrical heat evaporation and metallic heat conduction. These methods were described and illustrated in the lecture and the conditions under which they are best applied detailed. It appears that success attended the various methods adopted. The problem of evaporation of the liquid air from vessels in a vertical position is easier of solution than when the vessels are liable to be in other positions. The use of the vacuum containers when liable to movement from the vertical position would result in the liquid being splashed about, but by packing the interior with a suitable absorbent, this does not occur. Several inert materials were tested as to their adaptability. These included forms of charcoal, asbestos, sponge and siliceous earth, commonly called kieselguhr. The experiment showed that asbestos and the siliceous earth absorbed the largest amounts of liquid. Careful comparisons between these indicated very markedly that asbestos was by far the most economical material, since the charged substance has only two-thirds the weight of the siliceous material when carrying the same weight of liquid oxygen. These masses of absorbed oxygen when in a vacuum vessel retain a constant temperature and a constant rate of boiling, until almost the last trace of liquid is gone.

Liquid air, as usually obtained, is not uniform in composition, ranging between 34 per cent. of oxygen to almost 100 per cent. The former mixture boils at  $80^{\circ}$  absolute temperature, the latter at about  $90^{\circ}$ . The mathematical and physical data in regard to these problems are presented at considerable length.

In the early days the use of cooled charcoal was studied, and it was found that only when the charcoal was free from volatile substances could high efficiency be obtained. In this connection the American work as to the nature of charcoals, by Chaney and his associates, is of interest. Tests were made as to the efficiency of vacuum containers, and it was found that there is little advantage in increasing the capacity above about 30 kilos for storage purposes, at which size the limiting efficiency of about 5 per cent. loss of total capacity per day is reached. In aviation about 5 litres



would be the useful mean size for supplying three or four persons, even though there might be one or two days' delay between the delivery of the liquid and its use. H. L.

**Detection of Hypochlorites and Chloramins in Milk and Cream.**—These substances being now largely used in dairy work for disinfecting utensils, it is not at all unlikely that they may be added to milk intentionally, or be accidentally introduced. Philip Rupp, Dairy Chemist, Bureau of Animal Industry, has investigated the tests for such substances in market milk, and his results have appeared in a bulletin of the department. For sake of brevity he uses the term "chlorine" for the available chlorine in the compounds. The detection of such chlorine in water is easy, by means of the starch-potassium iodide or ortho-toluidin test, but in dealing with milk there are interferences owing to the union of the chlorine with the proteins. It was found, however, possible to liberate the chlorine so that it will react with potassium iodide. Mixtures of pure milk and cream were made with definite small amounts of hypochlorites and chloramins and set aside in an ice-box for 48 hours. These were tested for chlorine, allowed to stand for several hours at room temperature, returned to the ice-box for 48 hours and again examined. A flask of pure, untreated milk was employed as a control.

The reagents are:

Seven grams of potassium iodide in 100 c.c. of water. This should be fresh.

One hundred c.c. of concentrated hydrochloric acid are diluted with 200 c.c. of water.

One gram of starch is boiled in 100 c.c. of water and cooled.

Distilled water should be used.

The test is applied as follows:

Five c.c. of the sample are placed in a medium-sized test-tube, 1.5 c.c. of the iodide solution added, the mixture shaken and the color carefully noted. If no perceptible color change appears, 4 c.c. of the dilute hydrochloric acid are added and the curd thoroughly stirred with a glass rod flattened at the end. The color is again noted. The tube is then placed in water at a temperature of  $85^{\circ}$  C. and allowed to remain 10 minutes, the temperature being maintained at the original point. It is then rapidly cooled in water, and again examined for color. Finally, 0.5 to 1 c.c. of the starch solution is added to the liquid below the curd and the reaction noted.

Milk containing 1 part of chlorine to 1000 acquires a distinct reddish tint and at a dilution of 1 to 2500 is still slightly colored as compared with the control. This statement applies to both hypochlorites and chloramins. With 1 part of chlorine to 5000 parts of milk, the liquid acquires a pale yellow on addition of the iodide solution. These data relate to samples not heated during the test. When the heating is applied the delicacy of the reaction is increased, so that 1 part of chlorine in 50,000 parts of sample may be detected.



Milk kept in the ice-box for 48 hours still gives the test. When kept at room temperature the delicacy of the test is not so great. Milk pasteurized at 145° F. reacts like raw milk, 20 per cent. cream reacts like milk. It is best to examine carefully the curd and liquid below it.

H. L.

**Telephonic Speaking and Hearing.** MARAGE. (*Comptes Rendus*, Oct. 23, 1922.)—"This note leads to the same results as those indicated by Mr. Fletcher in the JOURNAL OF THE FRANKLIN INSTITUTE, June, 1922, page 729, of which a résumé appeared in the *Revue générale des Sciences* for September 15-20, 1922. This agreement is interesting because the processes employed are entirely different."

Known facts of experience—(1) The ear is much more sensitive to sounds of high than to those of low pitch, or less energy is needed to make audible a sound of high pitch than one of low pitch.

(2) No two ears are entirely alike because the cerebral auditory centres interpret the vibrations affecting the ear.

(3) Hearing is no more fatiguing than breathing or digesting. It is listening that causes fatigue, because then the brain comes into play.

Owing to the high pitch of their voices women and children have an advantage in making themselves heard over the telephone. But being heard is not enough. It is necessary for comprehension that vowels and consonants be clearly distinguished. From a photographic record of the word "bonjour," presumably pronounced by a Parisian, it is concluded that the duration of the consonants is only one-twelfth of that of the vowels. The consonants do not have in French a fair chance to produce an impression. When an analysis is made of "le roulement du tonnerre," pronounced by a person from the Midi, quite a different division of time is found. The duration of the consonants is to that of the vowels as 4 to 3. The writer draws, of course, for France, the conclusion "Other conditions being equal, for telephone operators, we should select inhabitants of the Midi who make their consonants to be heard as well as their vowels." One who has spoken with a man from Vaucluse might, however, doubt the wisdom of this suggestion.

Both the *d* and the *t* appear to have no detectable duration. "It is a rare thing to find among telephone operators a sense of hearing, I will not say fine, but even normal. Is this due to the fatigue produced by prolonged use of the telephone? Perhaps this is so, since there is in this occupation brain work very great in amount and all the greater because the public speaks too rapidly, pronounces badly and listens badly." All the above is related to the use of the telephone in speaking. In order to obtain data on transmission of the singing voice, Professor Marage had his pupils at the Sorbonne record their impressions of a concert given at the Eiffel Tower and heard by them by means of the wireless telephone. The



notes were very accurately transmitted. Men's voices are better understood than those of women. Resonators augmenting the volume of sounds at the same time modify them to a great extent.

G. F. S.

**The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current.** R. D. KLEEMAN. (*Phys. Rev.*, Sept., 1922.)—Porcelain slip is a colloidal solution in water of particles of flint, feldspar and clay. "During some experiments on the electric deposition of porcelain slip it was observed that the deposit obtained from the slip used in the wet porcelain process was solid though not quite dry, while that obtained from slip used in the dry process was of the consistency of thick cream. It was soon found that the difference in the nature of the deposits obtained was due to the small quantity of sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) that is mixed with the slip used in the wet process. It was found that besides sodium silicate the substances  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , H tartrate, Na tartrate, NaOH, KOH showed the effect very well, and in fact it was found that most substances showed the effect in a more or less degree." The compactness of the deposit in general increases with the quantity of substance added though with a small added amount (one part in from 300 to 1000 by weight), the maximum effect is attained, and further increase produces no noticeable result. The current density seems to be without effect on the hardness of the deposit, unless sufficient gas is evolved to interfere with the process.

There is a connection between the foregoing effect and the following. Let a slip be taken which holds 30 per cent. of solid matter by weight. To this add one three-hundredth of  $\text{Na}_3\text{PO}_4$ . Solid matter will be deposited, mostly feldspar and flint. This precipitate will, however, go again into solution upon the addition of further solid matter. When enough of this has been added to make the fluidity the same as before the introduction of  $\text{Na}_3\text{PO}_4$ , the slip will be found to contain about twice as much solid matter as before.

"Both effects may be explained if we assume that the radii of the spheres of action of the particles of the slip are diminished by the dissolved substance. It is concluded that the volume of the sphere of action of a particle in porcelain slip is about double the actual volume."

G. F. S.

**Progress in Nitrogen Fixation.**—The annual report of the United States laboratory for research on nitrogen fixation gives a summary of the work accomplished in the fiscal year ending June 30, 1922. The laboratory is under the direction of Doctor Cottrell, and is in the Department of Agriculture. The importance of the procedures for nitrogen fixation is pointed out. Three of these are at



present prominent: Direct union by the arc, production of cyanamide and synthesis of ammonia. Several others, Buchner (alkali-cyanide), Serpek (aluminum nitride) and Häuser (explosion) have been investigated and operated on fairly large scales, but cannot yet be considered commercially established. In the United States at present nitrogen compounds cannot be made by fixation at prices that will compete with Chile nitrate and ammonia from coal coking, except under unusually favorable circumstances. The special problem before the research worker in this field is to reduce the cost of the fixation methods. The synthetic ammonia (Haber) process is the one that presents especial advantages and difficulties. The principal difficulty is to secure a catalyst that may be easily obtained in quantity and that is not very sensitive to impurities. The laboratory has had considerable success in this line. The production of pure hydrogen and the discovery of a material for the containers have been also studied with encouraging results. Ordinary carbon steel soon deteriorates under the conditions in which the gases are combined. The development of apparatus capable of bearing a much higher pressure has been undertaken, inasmuch as combination is greatly favored by increasing pressure. Studies of the cyanamide method have not so far indicated any considerable reduction of cost. The arc method has the advantages that it can be installed rapidly and delivers the nitrogen directly in the oxidized condition. The direct cyanide (Buchner) method has not been successfully developed on a commercial scale. The chemical and engineering features require further study. There is some doubt whether the product of the cyanide process can be converted cheaply into fertilizing material, but it must be borne in mind that the recent application of hydrogen cyanide as a fumigating agent for fruit trees has developed a new and rapidly growing market.

Comparatively little information is at hand as to the agricultural value of many of the compounds obtained by nitrogen fixation, for which reason an experimental farm has been installed. Interesting and valuable results have already been obtained and are being prepared for publication.

H. L.

**On the Minimum Potential for Electrical Discharge in Gases at Low Pressures.** E. DUBOIS. (*Comptes Rendus*).—In a former investigation the author made known singular variations of potential found by him in studying electrical discharges in hydrogen at low pressure. At that time he attributed these to the presence of gas occluded by the electrodes. More recently he has used platinum, tungsten and molybdenum as electrodes and now he concludes that the variations of potential are to be ascribed to the occurrence of saline substances upon the electrodes.

Let the two electrodes be fresh pieces of the same metal (state A) and let the difference of potential for disruptive discharge be determined. Now let both electrodes be heated to white heat in a vacuum for several seconds. A greater difference will be subse-



quently required for discharge than was previously the case. If alternate heatings and measurements be made, it will be found that the difference of potential tends rapidly toward a limit corresponding to a new state of the metal (state B). For all three metals mentioned there is a potential difference greater by about 100 volts needed for discharge with state B than with state A. If one of the electrodes is in state A, while the other is in state B, it is the cathode which determines whether the higher or the lower difference of potential must be applied to get discharge.

The explanation offered by the author is that passage of a metal from state A to state B is due to the disappearance of some substances or mixture of substances from the cathode. The following experiment bears out this interpretation. Take two electrodes in state B. On one put traces of potassium chloride. Upon making this electrode the cathode the experimenter finds that the potential difference sinks to that corresponding to state A, but, if he makes the soiled electrode the anode, the P.D. for state B will be required for discharge.

To cause the difference of potential to decrease to a notable extent no more than a millionth of a gram of salt per sq. cm. is requisite on the cathode.

The number of volts measuring the difference of potential for discharge is the same within the error of experiment for all three metals in gases at the same pressure.

The nature of the metal, therefore, seems to make no difference. It is possible to make a metal pass from state A to state B by causing an intense discharge to pass between the electrodes for some time.

G. F. S.

**Note on Overblown Pipes.** S. BHARGAVA and R. N. GHOSH, Muir Central College, Allahabad, India. (*Phys. Rev.*, Nov., 1922.)—When an organ pipe is blown the fundamental tone is obtained when a certain pressure of air is used. If this pressure be increased, not only does the sound grow louder but its pitch likewise rises. At one pressure the octave of the fundamental is heard for the first time. As the pressure continues to increase this octave grows more and more prominent and later the pipe settles down to the production of this tone.

By means of a Phonodeik these Indian experimenters have measured the change of pitch with increasing pressure when the blowing lip was .8 cm. from the edge of the pipe, with the following results where pressures are given in heights of the water column and pitches by the frequencies of the tones: 6 cm., 490 (the fundamental); 10 cm., 495; 20 cm., 500; 32 cm., 505; 38 cm., 1050 (octave), and 50 cm., 1052. "At about 30 cm. of water the octave is clearly heard with the fundamental." The great rise in pitch from 32 to 38 cm. is due to the extinction of the fundamental at



the higher pressure. At lower pressures the octave is present, but it is subordinate to the fundamental.

Similar studies were made with the lip at different distances from the edge. In all the same succession of phenomena was noted. The greater the distance from lip to edge the higher the pressure requisite to elicit the fundamental, and the same is true for the octave. It requires six times as much pressure to evoke the fundamental when the distance is 5 cm. as when it is 1 cm., but for the octave the ratio needs to be made twenty for the same change of distances.

After the octave has been obtained, further increases in blowing pressure have but little effect in raising the pitch. The hydrodynamic problem related to the blowing of a pipe is by no means completely solved, but this modest contribution has helped to clarify certain features of it.

G. F. S.

**Evaluation of the Intensity of Vertical Electrical Currents Leaving the Surface of France.** C. MAURAIN and MRS. DE MADINHAC. (*Comptes Rendus.*)—Let a closed curve be traced on the surface of the earth. Around this contour integrate the expression  $H \cos\theta dS$ , where  $H$  is the horizontal component of the earth's magnetic field,  $\theta$  is the angle of this component with the contour and  $dS$  is an element of the contour. The integral should be zero, provided the magnetic field depends upon a potential. If it is not zero, the presence is indicated of an electrical current passing vertically through the surface embraced by the contour. The integration was applied to a part of France having an area of 415,100 sq. km. The integral was not zero but had a value showing a vertical current of 1800 amperes, or .0043 ampere per sq. km.

L. A. Bauer studying the same problem for the entire earth has inferred for regions between the north pole and latitude  $45^\circ$  north electrical currents directed upwards and of strength .026 ampere per sq. km., and, from the latitude named to the corresponding south latitude, currents flowing downwards of strength .010 ampere. France is not far from the latitude where these currents change their direction, hence their small value for this country.

G. F. S.

**Testing of Foodstuffs for Vitamins** is described by J. C. DRUMMOND and A. F. WATSON, of University College, London (*Analyst*, 1922, xlvii, 235-246). Physical and chemical methods do not exist for the detection and determination of the vitamins, so they must be studied by the biological method, *i.e.*, their action on animals. Fat soluble A, which promotes growth and prevents the eye disease known as xerophthalmia, accompanies the unsaponifiable fraction of a fat, provided the latter be isolated under conditions which exclude oxidation. A daily dose of approximately 0.01 milligram of this vitamin, as it occurs in cod-liver oil, is sufficient to produce nearly



normal growth in an albino rat. The traces of this vitamin, which occur in casein, are destroyed if that protein be spread out in thin layers and be exposed for several hours to a temperature of  $110^{\circ}$  C. in a current of air. In testing for water soluble B, determination of the growth curve of the rat is preferred to determination of the curative effect on a polyneurotic pigeon. Commercial yeast extracts are especially rich in this vitamin. In the past, food control officials have tested meat extracts for adulteration with yeast extract; in the future, they probably will have to combat adulteration of the vitamin-rich yeast extracts, with less potent materials. In testing for the antiscorbutic vitamin, water soluble C, use is made of the guinea-pig. Lemon juice is a far more potent antiscorbutic than lime juice.

J. S. H.

**A Resistance Furnace with Molybdenum Wire.** P. FLEURY. (*Comptes Rendus*, Nov. 13, 1922.)—A temperature of more than  $1700^{\circ}$  C. can be maintained in a cylindrical space several centimetres in diameter and several decimetres in length by sending the electric current through a spiral of molybdenum wire wrapped about a refractory, insulating support. This metal is preferred to tungsten, though it is more volatile and more fusible than the latter, because it is less costly, more lasting and easier to wind. The furnace was maintained in a vacuum. When the insulating material, alundum, was heated up for the first time, it disengaged gas that attacked the molybdenum. To avoid this the heating needed to be so slow that the gases could be removed as soon as they appeared. Thus at the first heating it took several days to attain  $1500^{\circ}$ . After this a much shorter time was required. The alundum is melted in this furnace, when the current gets too strong, but the metal wire stands the temperature well and can probably be raised to higher temperatures if supports of cast magnesia or zirconia be used.

G. F. S.

**Elasticity and Symmetry of Quartz at High Temperatures.** ALBERT PERRIER and B. DE MANDROT. (*Comptes Rendus*, Oct. 16, 1922.)—Certain hypotheses on the nature of piezoelectricity led one of the authors to predict the disappearance of this phenomenon in the case of quartz for some temperature. This was found by experiment to be  $576^{\circ}$  C. It remained to investigate the temperature relations of the elasticity of the crystal, the other element entering into piezoelectricity. Plates of quartz, from 70 to 80 mm. in length, were supported near the ends and weighted at the middle. Considerable difficulty was met in connection with the elevation of temperature and with the fragility of the plates at the temperature of transformation.

Young's modulus in kg. per sq. mm., parallel to the optical axis is 10,480 at  $18^{\circ}$ . As the temperature rises it diminishes at first slowly, then more rapidly as  $576^{\circ}$  is approached,  $572^{\circ}$ , 6960;  $574^{\circ}$ , 6510;  $574.5^{\circ}$ , 6320;  $575^{\circ}$ , 6020;  $576^{\circ}$ , 6680;  $577.5^{\circ}$ , 9060.



From this temperature onward the modulus continues to increase until it reaches the value of 9910 at  $1078^{\circ}$ . In directions perpendicular to the optical axis the effects of temperature are even more marked:  $18^{\circ}$ , 8010;  $573^{\circ}$ , 3570;  $574^{\circ}$ , 3210;  $576^{\circ}$ , 9030;  $585^{\circ}$ , 10,530;  $1140^{\circ}$ , 12,190.

With regard to the effects of both force and temperature upon the crystal a complete reversibility was found, except that near the transformation point several minutes were needed for the attainment of the figure of equilibrium.

In connection with the variations of the modulus with temperature it is interesting to note that up to the transformation temperature all dimensions of the crystal grow longer with rise of temperature, while above that point they contract.

A study of the modulus along two directions making  $50^{\circ}$  with the optical axis leads to the conclusion that at  $576^{\circ}$  the crystal passes from rhombohedral to hexagonal symmetry. G. F. S.

#### **Vapor Tension of Some Copper-zinc Alloys in the Solid State.**

L. GUILLET and M. BALLAY. (*Comptes Rendus*, Nov. 27, 1922.)—When brass is heated, the volatilization of the contained zinc begins. This is found to be greatly influenced by the nature of the surrounding gas, whether oxidizing, neutral or reducing. A brass of composition, copper 55.20 per cent., zinc 44.75 per cent., iron .02 per cent., was used. This was heated for six hours in different gases circulated in the same manner. With air .15 per cent. of the weight of the specimen was lost when the temperature was kept at  $650^{\circ}$  C. and 1.19 per cent. when at  $800^{\circ}$ . A film of oxide formed and hindered the process of volatilization. In nitrogen at the temperature of  $800^{\circ}$  the loss was 7.88 per cent., in CO at  $808^{\circ}$  10.58 per cent., in hydrogen at  $800^{\circ}$  10.57 per cent., and in the same gas at  $600^{\circ}$  only 1.09 per cent.

The vapor tension of the solid brass in millimetres of mercury was found to be 3.33 at  $540^{\circ}$ , 5.09 at  $560^{\circ}$ , 6.90 at  $575^{\circ}$ , 11.20 at  $600^{\circ}$  and 19.30 at  $630^{\circ}$ . G. F. S.

**The Effect of Temperature on the Scattering of X-rays by Crystals.** G. E. M. JAUNCEY. (*Phys. Rev.*, Nov., 1922.)—When X-rays are regularly reflected from the surface of a crystal, a part of the incident beam is at the same time diffusely scattered. A crystal surrounded by a heating box having mica windows received on one of its faces a beam of X-rays from a Coolidge tube. The strength of the diffusely reflected beam was measured by an ionization chamber. Observations were made with the crystal at  $17^{\circ}$  C. and again at  $295^{\circ}$  C. For rocksalt the scattered intensity at the higher temperature was 1.33, or 1.18 times as great as at  $17^{\circ}$ , according to the angle at which the scattered radiation was received. For calcite the change of temperature made little or no difference. The results are in only very crude agreement with Debye's theory of this effect. G. F. S.



**A Boat Which Sails into the Teeth of the Wind by Using the Wind Itself as Motive Power.** CONSTANTIN, JOESSEL and DALOZ. (*Comptes Rendus*, Oct. 23, 1922.)—Sails will not suffice for this. The solution was found by using an air turbine geared to a screw in the water. The combination was mounted on a fishing boat. The air turbine, with two blades and devised for minimum weight, was 9 m. in diameter. The screw had four blades and was 1.05 m. in diameter. In both the inclination of the blades was variable. The setting of the turbine perpendicular to the wind was made by the steersman through an endless screw gearing. "The boat thus equipped showed itself very manageable. One man was enough to bring it from Sevres to Saint-Cloud in the midst of the active shipping of the Seine and in spite of the current of the river. It could be handled in just the same way as a boat with a thermal motor." The boat could progress in any direction to the wind.

The wind acting on the turbine located a considerable distance above the water produced a force tipping the boat over. This was counteracted by a deeper keel.

It might seem that the forward thrust of the screw could not be greater than the backward push of the wind on the turbine. With suitable dimensions of the turbine and screw and with a proper transmission with multiplication of the angular velocity of the former to the screw, the forward thrust may, however, be made the greater.

G. F. S.

**The Electric Arc as Rectifier.** STANISLAW BOROWIK. (*Physikal. Z.*, Sept. 15, 1922.)—In studying the alternating current arc it was found that an arc, one of whose electrodes was covered with iron oxide while the other was carbon, allows only that phase of the alternating current to pass for which the oxide is positive. This phenomenon regularly manifested itself for current strengths ranging from 2 to 30 amperes and for voltages from 100 to 1500. Somewhat similar results were obtained for the current from an induction coil.

It is interesting to note that this paper comes from a laboratory in Petrograd.

G. F. S.

**Distribution of Methyl Anthranilate in Grapes.**—Power and Chesnut showed some years ago the existence of this ester in many samples of grape-juice and devised methods for its detection. They have extended their researches in order to determine whether the ester occurs in all forms. Their results have just been published in *Jour. Agric. Res.* (1923, v. 23, 47). Although the cultivation of the vine and the utilization of its juice for the manufacture of an intoxicating beverage dates from the earliest period of which we have written history, the genus *Vitis* is more developed in the New than in the Old World. The Old World vine is *V. vinifera* L. and even at this day, this species, developed into many varieties, is exclusively cultivated. The most commonly cultivated American species is



*V. labrusca* L, a typical representative of which is the Concord grape. Another form much esteemed is *V. riparia* Michx, which is the original of the Clinton grape. In the South, *V. rotundifolia* Michx, best represented by the Scuppernong or Muscadine, and *V. æstivalis* Michx, represented by the Norton grape, are principally in use.

Authentic samples of grapes from many sources were tested, and it was found that when the plant was derived from *V. labrusca* or hybrids in which this predominated, methyl anthranilate was present, but the fruit of *V. vinifera* does not give evidence of it. It appears that this species does not thrive in the United States, east of the Rockies, but is very successfully cultivated in California. The great grape-growing industry of that region is said to depend upon the cultivation of the European species. The literature of grape-culture shows that about 6000 varieties have been described. Even in California, however, many of the vines are growing as grafts on American roots, and it is thought probably that in time all the vines will be thus grafted. A number of samples of commercial grape-juice were tested, most of which contained the ester.

H. L.

**Oxidized Kerosenes as Fuel.**—This problem has been undertaken at the laboratories of Carnegie Institute of Technology, Pittsburgh, in experiments to determine the relative efficiency of kerosenes and oxidized kerosenes as fuels. According to a report by Dr. J. H. James, Head of the Department conducting the experiments, oxidized kerosenes cause less “knocking” tendencies than the straight when used in a kerosene engine, but have approximately the same power development notwithstanding that the thermal value is one-eighth less. Doctor James attributes this efficiency to the better “clean up” in the combustion of them.

The experimental work at Carnegie gives promise that oxidized kerosene, which is manufactured by catalytic oxidation from low-grade petroleum, may become a useful fuel.

H. L.

**Studies of Vitamins.**—At a recent meeting of the Royal Institution of Great Britain, Dr. Arthur Harden presented a summary of present knowledge on the question of vitamins. Experiments on these substances are difficult and tedious. It seems to be established that vitamins A and C are fairly resistant to moderate increase of temperature provided air is excluded, but deteriorate rapidly when exposed to oxidation. Vitamin B is less affected by heat and aeration. All three vitamins originate in the vegetable kingdom, and in view of this fact, it is interesting to recall the Biblical endorsement of the “green herb for meat” as given to the residents of Gan-Eden. In fats, the vitamin seems to reside entirely in the unsaponifiable portion, and as this usually consists largely of cholesterol, which has no value, it is evident that the amount of the really active substance is very minute. Vitamin A does not appear until the photosynthetic actions occur. Vitamin C is not in seeds, but appears when they



germinate and before any green parts are formed. The conditions under which vitamin B is produced are still somewhat uncertain, but its existence in yeast shows that it may be produced without action of light. Milk from stall-fed animals is poor in A and also likely to be deficient in C. The comparatively enormous amount of A in cod-liver oil has been one of the most striking results of recent investigations, but in connection with these data the fact that liberal exposure to sunlight will often counteract certain dietetic deficiencies must not be overlooked. It must not be forgotten that most of these feeding experiments are conducted in laboratories not open freely to sunshine and that the animals are under decidedly unnatural conditions in some ways. H. L.

**The Radioactivity of Springs Near Bagnoles-de-l'Orne and Its Relation to Geological Structure.** P. LOISEL. (*Comptes Rendus*.)—This region is about 100 miles west of Paris. The springs occur in groups distributed along lines running from northeast to southwest and following the general structural lines of the region. Those springs, whose radium content is greater than one millimicrocurie per litre, with a single exception, are arranged along a syncline of sandstone. To the south of these is a second group, emerging from granite and containing less radium than the first. Still further to the south is a third group with even less radium content. To the north of the first group the radioactivity grows less with increasing distance from this group. In the extreme north of this region is a spring with a high content of 1.83. The cause of this anomaly is not yet known. Those springs whose waters come from merely superficial layers have only a slight radioactivity or none at all. In the chief spring the content in a year diminished to .735 from .980 millimicrocurie per litre. The effect of rain is to cause a prompt increase in the radium content.

There appears to exist a close connection between the geological formation from which the spring issues and the radioactivity of its waters. G. F. S.

**Lightning and Trees.** V. SCHAFFERS. (*Comptes Rendus*, Nov. 27, 1922.)—In order to explain the immunity from strokes of lightning enjoyed by certain species of trees recourse has been had to the quiet, preventive discharge that takes place because of the pointed or jagged form of the leaves or because of the hairs growing on the leaves. The author conducted a series of experiments to determine the effect of leaves on the electric discharge. A healthy leaf, freshly picked, was placed 2 cm. from an insulated disc charged positively by an electrical machine. Both the leaf and the negative terminal of the machine were joined to earth. The potential difference was raised until the silent discharge set in between leaf and plate. The values range in volts from 3190 for acacia to 10,550 for alder. Statistics of the relative numbers of different species of trees struck by lightning in Belgium and



also in Styria and Carinthia are given, but there seems to be little or no parallelism between these statistical results and the proportions that might be expected to hold in view of the experiments. It is true that alder leaves require the highest potential difference and might for this reason be expected to experience the least protection as a result of the silent discharge and therefore to be struck most frequently. As a matter of fact they were but rarely struck either in Belgium or in Austria. This may be due to the low height attained by the tree. In Belgium poplars were struck eight times as frequently as resinous trees, while in the two Austrian provinces resinous trees were struck four times as often as poplars.

When grass was substituted for leaves in the experiment, 2490 volts only were needed, whereas the gilded points of a lightning rod required from 8510 to 9810 volts.

G. F. S.

**A Study of the Effect of Adsorbed Gas on the High-frequency Resistance of Copper Wire.** AUSTIN BAILEY. (*Phys. Rev.*, August, 1922.)—"At very short wave-lengths, measurements made of the high-frequency resistance of a one-metre square loop of wire show a much larger value than that calculated from the formula for the resistance of a straight wire of the same length." For 18 B. and S. gauge copper wire the measured resistance for waves 30 m. in length is more than three times as great as that calculated from the formula. Since in accordance with the skin-effect a large part of the current will flow through the peripheral portions of the wire, any modification of those parts will be of significance in connection with the discrepancy in resistance.

"A square loop, 60 cm. on a side, was formed by enclosing copper wires inside of glass tubes connected to a vacuum pump, and after several hours' preliminary heating and pumping, the wire was glowed, and then its resistance for radio-waves of 20 metres' length was found to increase in 20 minutes by several per cent., though the residual pressure was only  $10^{-5}$  atm. After successive glowings the effect became progressively less as the oxide layer disappeared. With higher pressures the increase to an equilibrium value came more rapidly. These results indicate that the gas adsorbed by the copper-oxide layer does increase the resistance, and suggest that possibly copper wire, whose surface is covered with a thin layer of metal such as tin, might have a lower high-frequency resistance than oxidized copper wire of the same size." Such a covering metal should neither oxidize readily nor adsorb gases.

G. F. S.

**Practical Applications of Ultra-violet Light.**—Considerable difference is observed as to the fluorescence of substances under ordinary light and light not visible to human eyes. Studies have been made by several observers, those published a few years ago by Wood having been among the most interesting. The most recent investigations are those made in the laboratory of physical chemistry at the University of Upsala, an account of which appears in the current



issue of the *Photographic Journal* (1923, vol. 63, 30). The work was carried out by Svedberg and Andersson. In 1915, Kögel worked out a method of deciphering palimpsests by taking advantage of the fact that the portions of the parchment on which erasures had been made do not fluoresce under ultra-violet rays as do the unaltered portions. A palimpsest is a manuscript from which the first writing has been removed by mechanical means and the sheet then written over with new matter. Several very valuable manuscripts have been treated in this way and the recovery of the original text has been very desirable. An important manuscript in the library at Upsala was lately photographed by Svedberg and Andersson by illuminating the sheet with two quartz lamps giving about 3000 c.p. each enclosed in light-tight houses, provided with windows glazed with Wratten UV filters. As the intention is to photograph the sheet with the fluorescent light emitted from it after the impinging of the ultra-violet rays, the camera lens was protected by a cell containing quinine sulphate solution with some hydrochloric acid, the latter being added to depress the fluorescence of the quinine salt. The details of exposure and the composition of developer are given. The MS is written with silver and gold letters on a purple dyed parchment. The exposure was only two minutes, while with common light an exposure of 300 minutes would be required.

Comparisons of the transmitting powers of the Zeiss UV glass and the Wratten filters were made, and the latter was found to be better adapted to practical work. It is evident that a wide field of investigation yielding both practical and theoretical results is here opened.

H. L.

**On the Flow of Liquids under Capillary Pressure.** E. K. RIDEAL. (*Phil. Mag.*, Dec., 1922.)—"The rate of penetration of liquids into capillary porous materials, of importance not only in biochemical problems, but also in the study of the phenomena of adsorption by materials such as charcoal and substances constituting the membranes of semi-permeable osmometers, has attracted but little attention." To put the problem in concrete form, let a long capillary tube be mounted horizontally with one end open to the air and the other sealed into a vessel containing just enough liquid to cover the mouth of the small tube. Let the liquid be sucked out into the capillary and forced back by compressed air so that the inner walls of the tube be thoroughly wet. At a time when the liquid has been brought well back in the small tube toward the vessel, let external forces be removed. At what velocity will the liquid travel outward through the tube under the action of the forward pull of its meniscus and of the retarding force due to its viscosity? A solution is found in which the velocity is expressed as the sum of a series, which for small values of the radius of the tube reduces to the form already given by Washburn. The square of the velocity equals the time multiplied by a fraction whose numerator is the product of the surface tension by the radius of the tube and whose denominator is



twice the coefficient of viscosity. The square root of this fraction bears the name of "penetration coefficient." The rate of flow was measured by a stop-watch for water and chloroform and for a series of alcohols. When the rate computed from the formula is compared with the observed value excellent agreement is found to exist, especially in the cases of water and chloroform, where the values of the constants needed for calculation are known with accuracy.

G. F. S.

**The Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Bisulphide with the Temperature.** E. E. HALL and ARTHUR R. PAYNE. (*Phys. Rev.*, Sept., 1922.)—From 1856, when Jamin began the study of the change of the indices of refraction of liquids produced by changes of temperature, the commonest of all liquids has been investigated in this regard, yet but two men have examined the range above 50° C. These, Ruhlman and Kettler, are not always in agreement and, hence, it seemed to repeat the measurements, using all the devices suggested by experience. The temperature of the water was kept constant to .1 degree and an electrically driven stirrer was used to secure uniformity of temperature. "The stirrer and the interior of the brass prism were heavily gold plated. It was found that enough brass would dissolve in the water in the course of a few hours to change the index of refraction by approximately two units in the fourth decimal place." Special care was used to have the liquid free from gases as well as from other impurities.

A spectrometer was employed for the measurements. These for water extended to 98.4°. The index of refraction for water relative to air is at 16°, 1.33333 and at 100°, 1.31783. The rate of change of the index per degree is -.00008 at 15°, but has grown to nearly four times as much at the boiling point. As an illustration of the accuracy with which such measurements have been made it is to be noted that the index at 30° was found by Walter in 1892 to be 1.33194, by Baxter, Burgess and Daudt in 1911 to be 1.33190, while the present authors furnish a result exactly midway between these other two.

G. F. S.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

---

Vol. 195

APRIL, 1923

No. 4

---

## UNSOLVED PROBLEMS OF COSMICAL PHYSICS.\*

BY

W. F. G. SWANN, D.Sc.,

Professor of Physics at the University of Minnesota.  
Associate Editor.

I HAVE heard it said that Rowland, when asked for advice by a student whose apparatus had failed to give the expected result would reply "Do something to it until something happens." Every experimentalist will recognize the wisdom of the counsel; but, alas, the student of cosmical physics is unable to avail himself of it to any great extent. There is little that he can do to much of the apparatus with which he deals, to the sun, the stars, and the planets: He can only wait and see what happens. How he would like to inclose our globe and its atmosphere in a lead casing several metres thick, and see what change is thereby produced in atmospheric electric phenomena, or reverse the direction of rotation of the earth, and study the changes in the earth's magnetic field for a few million years. As he would find it difficult to discover anyone willing to finance either of these projects, however, there is nothing for him to do but wait, observe what he can, duplicate nature's processes, as best he may, on a small scale in his laboratory and above all things, think hard.

---

\* Presented at the Stated Meeting of the Institute held Wednesday, December 20, 1922.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.

VOL. 195, No. 1168—31

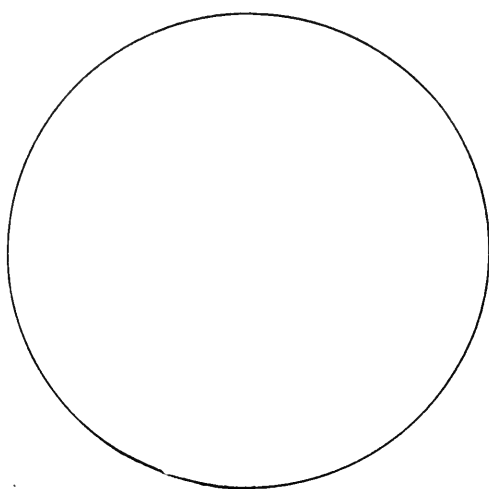
433



**ATMOSPHERIC ELECTRICITY.**

Fig. 1 represents a circle. The thickness of the line is not great, yet that line represents in relation to the size of the earth as represented by the circle, a shell seven times as thick as that to which practically all of our atmospheric electric observations are confined. Within this region we know that there is an electric field which is perpendicular to the surface of the earth, and that it is brought about by a negative charge on the surface and a positive charge in the atmosphere. The field amounts to about 150 volts per metre at the surface, and goes through fairly regular vari-

FIG. 1.



ations throughout the day, and throughout the year, changes of the order of 50 per cent. or more of its value. It diminishes with altitude until at an altitude of about 10 kilometres it attains a value insignificant compared with that at the surface.

**ATMOSPHERIC CONDUCTIVITY.**

Now the atmosphere is a very feeble conductor of electricity, so that the positive charge in the atmosphere tends to become neutralized by the negative charge on the earth. The conductivity of the atmosphere is produced by the presence in it of charged molecules of nitrogen and oxygen, called ions. These, in virtue of their charge, move in an electric field and give up their charges to bodies which they encounter, thereby discharging them. Under ordinary conditions there are about 1000 of each sign of ions in



each cubic centimetre, a very small number compared with the 30 million million million molecules of air which that cubic centimetre contains. The positive ion is produced by detaching from the neutral molecule one of those electrons which modern physics has taught us to regard as one of the fundamental constituents of all matter. The negative electron attaches itself sooner or later to some neutral molecule and, thus loaded, constitutes the negative ion. The ejection of the electron from the atom is brought about by some external agency. Of these there are principally three kinds, all of which are represented in the radiations shot out from a substance like radium, which is in a state of continual spontaneous disintegration.

First there is the alpha particle, a positively charged atom of helium, moving with a speed of 18,000 miles per second. Then there is the beta ray, which is simply a negative electron moving with a speed approximating that of light. Finally we have the gamma ray, which is a kind of wave motion in the æther. When an alpha ray approaches an atom, it tends to snatch away an electron, just as a comet coming into our solar system might tend to snatch away the moon. The beta ray tends to hurl the electron out by repulsion, just as a comet fitted with a huge air blast might tend to blow the moon away. Finally the gamma ray acts by setting up a sort of agitation in the æther, in virtue of which the electron acquires a velocity great enough to enable it to leave the atom.

A large portion of the ionization, and consequently of the conductivity of the atmosphere is produced by the presence in it of radium emanation. A cubic centimetre of the atmosphere contains only about one and a half molecules of emanation while it contains about 30 million million million molecules of air; but, this emanation is nevertheless sufficient to contribute quite appreciably to the ionization. The alpha, beta and gamma rays from the radioactive emanations in the air, the gamma rays from the radium in the soil, and a possible penetrating radiation of cosmical origin constitute the main sources of ionization in the atmosphere. The fact that the ionization over the great oceans, where there is no radioactive material, is comparable with that over land, suggests that the cosmical radiation may play an important rôle, although recent experiments have thrown some doubt upon the reality of



this radiation, at least as regards its presence at low altitudes. Thus to sum up the situation, certain rays, alpha, beta, and gamma rays, and possibly certain cosmical rays, are responsible for the ejection of electrons from a few molecules of the air, thus resulting in the production of positive and negative ions, which render the atmosphere conducting.

The conductivity of the atmosphere at the earth's surface is extremely small compared with that of such a substance as copper. Thus a cylinder of air one inch long offers as much resistance to the flow of the electric current as would a copper cable, of equal cross-section, reaching from here to the star Arcturus and back twenty times over. Nevertheless, this conductivity is sufficient to insure that 90 per cent. of the earth's charge would disappear in ten minutes were there no means of replenishing the loss. The explanation of the maintenance of the earth's charge is the great problem of atmospheric electricity. The replenishment to be accounted for is not large. The total current from the whole of the earth's surface is only about 1000 amperes, or as much as is taken by 3000 incandescent lamps; but, our knowledge of the nature of electrical phenomena is sufficiently definite to place very critical restrictions upon any process which we may imagine for the replenishment.

#### THE MAINTENANCE OF THE EARTH'S CHARGE.

It is obvious that if negative electricity is leaving the earth, or positive electricity entering it in virtue of the potential gradient operating in a conducting atmosphere, any compensating stream of electricity must take place by processes which operate in opposition to the electrical forces of the field. The theories which have been proposed divide themselves for the most part into two classes, those in which gravity is the primary agent instrumental in moving the charges against the field, and those in which the return of negative corpuscles to the earth is brought about in opposition to the field through the agency of a very high velocity produced in them by some means or other.

*Theories Invoking Gravitation.*—As an example of the former class we have the theory of Mr. C. T. R. Wilson, to the effect that the replenishment takes place through the agency of rain. Theoreti-



cal considerations have been thought to suggest that the rain-drops should form on the atmospheric ions, and more copiously on the negative than on the positive ions, so that rain might be expected to be, on the whole, negatively charged. The charged drops, falling to earth under gravity, would do so in opposition to the electric field, and would constitute the replenishment. This theory is open to two primary objections. In the first place, while rain is charged, and to a degree probably sufficient to account for the necessary replenishment, it is found that 90 per cent. of the rain which falls is *positively* charged. Again, it appears that there are grave theoretical difficulties concerned with the possibility of condensation of water upon atmospheric ions, in the form of drops of appreciable size, so that this theory is now generally discarded.

A theory which came near to being successful, and which undoubtedly plays a part in the origin of the earth's charge is one due to Ebert. Ebert's theory, which constitutes a modification of an earlier theory due to Elster and Geitel, invokes the fact that if ionized air be passed through a fine tube, the negative ions diffuse to the walls of the tube more rapidly than do the positive ions, so that the air which emerges from the tube is positively charged. Ebert applies this to the atmospheric electric problem, by supposing that the air which is to be found in the interstices of the soil, and which is ionized by the radioactive material therein, is drawn out during the periods of falling barometric pressure, leaving an excess of negative charge on the walls of the interstices. The positive charge which emerges would be held in the immediate vicinity of the ground by the negative charge, but here Ebert invokes the aid of upward air currents, which carry it, against the field, into the higher regions of the atmosphere. The theory has been criticised on the basis that the emission of ions from the ground would be insufficient, and the upward currents too feeble. I think, however, that one of the most serious objections is to be found in a conclusion, which follows comparatively simply from theoretical considerations, to the effect that, on such a theory, it would result that, before the ascending positive charge had risen to an altitude of a kilometre or so, it would have disappeared almost completely, devoured as it were by the negative charge continually fed into it from the earth below, through the medium of the con-



ducting atmosphere.<sup>1</sup> We should obtain a positive charge in the atmosphere, a negative charge on the earth's surface, a conduction current and a potential gradient; but, all of these phenomena would be confined to a layer of the atmosphere about a kilometre or so in thickness. The whole of the positive charge in the atmosphere would be found in this layer, and, being equal to the negative charge on the earth's surface, since that was formerly its partner in neutrality, it would annul the field at all greater altitudes.

Certain other difficulties present themselves in the theory of Ebert, and in the precipitation theory of C. T. R. Wilson. Thus, in the case of both theories, the corresponding positive and negative charge densities would remain sensibly in the regions in which they originated, with the result that there would be no electric field at other parts of the earth. It is useless to invoke the winds for the transportation of the atmospheric positive charge to remote regions, for 90 per cent. of it would disappear in ten minutes in the course of its journey on account of the conductivity of the

---

<sup>1</sup> The reason is as follows: Let  $\rho$  be the density and  $v$  the velocity of the ascending positive electricity. Let  $X$  be the potential gradient, and  $\lambda$  the conductivity at a point in the atmosphere; and let the axis of  $x$  be taken vertically upwards from the earth's surface.

The equilibrium between the conduction and convection current at all altitudes requires that

$$\rho v + X\lambda = 0 \quad (1)$$

Poisson's equation gives

$$\frac{\partial X}{\partial x} = 4\pi\rho \quad (2)$$

so that, from (1) and (2),

$$\frac{v}{4\pi} \frac{\partial X}{\partial x} + X\lambda = 0$$

which gives

$$X = X_0 e^{-4\pi \int_0^h \frac{\lambda}{v} dx} \quad (3)$$

where  $X$  is the potential gradient at the altitude  $h$ .

Now, since  $\lambda$  increases with altitude and  $v$  decreases, the value of  $X$  as given by (3) is certainly less than the value obtained by substituting in it the surface value of  $\lambda/v$ ,  $\lambda_0/v_0$ .

Thus,

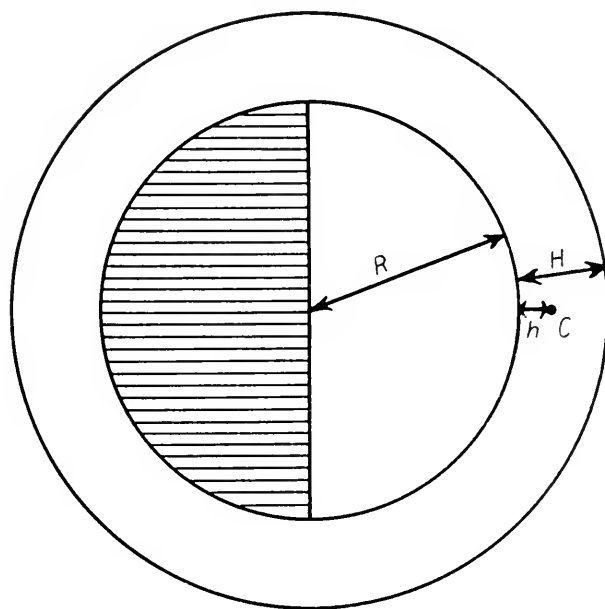
$$\frac{X}{X_0} < e^{-4\pi \frac{\lambda_0}{v_0} h}$$

If  $\lambda_0 = 3 \times 10^{-4}$  e.s.u., and  $v_0 = 100$  cm./sec., and if we put  $h = 1000$  metres, we find that the value of  $X/X_0$ , at this altitude is less than 0.02.



atmosphere. Difficulties of this kind confront any theory in which the replenishment of the charge takes place by the separation of charges at isolated places in such a manner that the complementary positive and negative parts are to be found comparatively near together. They become much less serious if we adopt the likely hypothesis that the lower atmosphere is surrounded by the equivalent of a conducting shell. Such a shell seems necessary to account for the reflection of wireless waves around the earth, and there is strong reason to suppose its existence on the basis of our knowl-

FIG. 2.



edge of the mechanism of the variations in terrestrial magnetism, to which I shall presently refer.

In the presence of such a layer, the action of a charged cloud is to set up a difference of potential between the layer and the earth, which difference of potential is handed round, as it were, to all parts of the earth, in view of the fact that the difference in potential between the earth and the layer must be the same at all places. A detailed consideration of the action of such a layer shows<sup>2</sup> that, if a charged cloud  $C$  (Fig. 2) is to be found at an altitude  $h$  above the earth's surface, and if  $H$  is the altitude of the conducting layer, and  $R$  the radius of the earth, the hemisphere of the earth, which is symmetrically remote from the charged cloud (the shaded hemisphere in Fig. 2), would receive  $R/H$

<sup>2</sup> The full theory of this matter will be given in a subsequent publication.



times the number of tubes of force which it would receive in the absence of the layer, and  $h/H$  times the number which it would receive if the charge on the earth and the charge on the cloud were pasted uniformly over the earth and atmosphere respectively. Thus, if rain should fall from a cloud at an altitude of 5 kilometres, and if the effective altitude of the conducting layer were 50 kilometres, the average contribution to the potential gradient on the shaded hemisphere would be one-tenth of what it would have been if the charges had been uniformly distributed over the earth and atmosphere, and over a hundred times as great as it would have been in the absence of the conducting layer. By the aid of such a conducting layer, we thus see how every centre of separation of charge, such as a rain storm, can pay a contribution, positive or negative as the case may be, to the general potential gradient at every part of the earth.<sup>3</sup>

However, even though difficulties attending the localization of the potential gradient be removed by the postulation of the conducting layer, there yet remain the others of which we have spoken, and which are sufficiently severe to make it improbable that the Ebert theory can figure as the main cause responsible for the earth's charge.

*Corpuscular Theories.*—Turning now to theories in which the replenishment of the charge comes about by the agency of high-speed electrified corpuscles shot into the earth, the first of these was proposed by G. C. Simpson. In this theory it was supposed that the sun emitted negative and positive corpuscles of high penetrating power. The former were supposed to pass right through our atmosphere and charge the earth, while the latter were of less penetrating power, and were caught in the atmosphere. In this way, the earth would continually receive negative and the atmosphere positive charge. The ordinary processes of atmospheric con-

---

<sup>3</sup> It may be remarked, moreover, that this action of the conducting layer minimizes slightly that objection to the Ebert theory which is founded upon the impossibility of the positive charge reaching altitudes greater than a kilometre or so. For, even such a small separation in the region of replenishment makes its own small contribution to the potential gradient at other places, through the medium of the conducting layer, and the contributions in these places will be of perfectly normal type, the variations with altitude being determined only by the nature of the variation of conductivity with altitude, and in such a manner as to keep the vertical conduction current density independent of altitude.



duction, would, moreover, cause a continual conduction of electricity between atmosphere and earth, so that a steady state would be reached when the amount of neutralization of charge by this latter process just balanced the charging effect due to the influx of the corpuscles. This theory requires that we suppose the existence of corpuscles of penetrating power so great that they could pass through the whole of the earth's atmosphere, which is equivalent in absorbing power to a column of mercury about 76 cm. high. The greatest range which has been observed in air, for the beta rays of radium, is about seven or eight metres. Electrons having a velocity of 99 per cent. of that of light can travel through only 1.3 cm. of aluminum, which is equivalent in absorbing power to about ten metres of air at atmospheric pressure.

TABLE I.

*Showing Variation of Average Range with Velocity.*

$\frac{\text{Velocity of corpuscle}}{\text{Velocity of light}}$	Average Range Metres.
0.80	0.7
0.85	1.1
0.90	1.9
0.95	3.5
0.99	10.5
0.996	18.0
0.998	26.0

Although, according to electromagnetic theory, the velocity of light represents the maximum velocity which a corpuscle can attain, one must guard against the supposition that, because corpuscles with velocity 99 per cent. of that of light have ranges of only ten metres in air, no corpuscles can have ranges much greater than this. For, electromagnetic theory shows that corpuscles with velocity even 99 per cent. of that of light are very far removed in their properties from those which approach that limit much more closely. As a matter of fact, the mass of a corpuscle increases with its velocity in such a way that the corpuscle must have infinite energy in order to attain the velocity of light. A theory of the absorption of electrons in matter, for high velocities, has been worked out by N. Bohr, and Table I gives, for different velocities approaching that of light, values of the ranges calculated on the basis of Bohr's formula, taken in conjunction with the experi-



mental values obtained by R. W. Varder for the lower velocities up to 0.99 of the velocity of light. On Bohr's theory, the range theoretically attains an infinite value for a velocity equal to that of light. As a matter of fact, for velocities approaching that of light much more nearly than those cited in Table I, additional considerations, which we shall presently discuss, become involved; but, the nature of these considerations is such as to result in ranges even greater than those assigned by Bohr's formula.

A theory such as that of Simpson has interesting consequences in respect of the variation of atmospheric current density with altitude to which it would lead. The ideas in this connection can be most simply studied by considering a case where the whole of corpuscular current through the troposphere is one of negative corpuscles, the positive carriers being caught in the upper atmosphere.

It is of course obvious that, in the steady state, the downward corpuscular current density must equal the upward conduction current density at each point of the atmosphere. Now if the corpuscles are absorbed at all as they descend, the downward corpuscular current density will decrease with approach toward the earth's surface, so that the upward conduction current density will increase with altitude. If, for example, the corpuscular current density should diminish from a certain value at 10 kilometres to half that value at 5 kilometres altitude, the conduction current density would have to increase by 100 per cent. over an increase of altitude from 5 kilometres to 10 kilometres. Our data on the variation of the vertical conduction current density with altitude are not very copious; but, as far as they go, they indicate no very great change with altitude. We thus see that the degree of penetration required by such a theory as that of Simpson is greater than would be necessary to merely account for the corpuscles reaching the earth. It must also account for their reaching with an absence of absorption compatible with the constancy of the conduction current density with altitude.<sup>4</sup>

---

<sup>4</sup> In so far as the positive corpuscles are absorbed more readily than the negative corpuscles, the inclusion of the former in the argument tends to reduce the rate of diminution of the net corpuscular current density as we descend into the atmosphere from above. Only under very special circumstances would the laws of absorption of the two kinds of corpuscles be such as to make the net corpuscular current density independent of altitude, however.



One might feel more satisfied if he could devise a theory which did not involve such a high degree of penetration as that required by Simpson's theory. There are one or two ways in which we can do this. Suppose we imagine that, owing to radioactivity or some other cause, a certain number of molecules of the air break up per second with the emission of a high-speed negative corpuscle. Then, although these corpuscles may be emitted, on the average, in all directions, the earth will receive some corpuscles from the atmosphere, and it will consequently charge up until the conduction current back to the atmosphere balances the corpuscular current. Practically all of the corpuscles received by the earth will come from a distance comparable with the average range of a corpuscle. We can secure the necessary replenishment with as short a corpuscular range as we wish, provided that we are willing to assume a sufficiently large emission of these corpuscles from each cubic centimetre. Unless we assume a fairly great range, however, we shall encounter difficulties in respect of the variation of the conduction current with altitude. Thus suppose that the average range were 10 metres, so that practically all the corpuscles which came to the earth came from a layer comparable in thickness with this amount. At an altitude comparable with 10 metres the resultant corpuscular current would be zero, because as many corpuscles would be shot upwards from the air below as were shot downwards from the air above. The corpuscular current would, in fact, increase from a maximum at the surface of the earth to zero at this altitude, as would also the conduction current and the potential gradient.

We thus see that if we were to have an equal emission of corpuscles from each cubic centimetre of the atmosphere, and an equal reduction of range in each centimetre of path, it would be practically necessary to assume an average total range equal to the altitude to which we wished to account for a potential gradient. The same result follows if we postulate a definite emission from each *gram* of the atmosphere, for then, although the pressure and density decrease as we ascend, the range increases in like proportion. We can escape from this unwelcome conclusion by postulating an increase of emission per gram with altitude, such as we should have if we were to imagine the emission brought about by some external radiation which was gradually absorbed as it descended. In fact, in order to obtain a constant conduction cur-



rent density, it would be necessary to postulate an increase of emission with altitude, comparable with twice the required corpuscular current, within a weight of air corresponding to the average range of the corpuscles.

It may be of interest to consider the orders of magnitude involved in a theory of this kind. It turns out that if the range is assumed to be 5 kilometres, it is only necessary to suppose that about one corpuscle is emitted per second from every 200 c.c. Now we know that about 6 ions are produced per c.c. per second, so that it is only necessary to suppose that one out of 1200 of these ions is produced with the ejection of a high-range corpuscle.

We may avoid the assumption of a spontaneous emission, and provide for certain other advantages by adopting a hypothesis which bears some resemblance to the foregoing. It has been customary to suppose that our atmosphere is traversed by a very penetrating radiation coming either from the outer regions of the atmosphere, or from some cosmical source such as the sun. This supposition has been invoked to account for the production of ions which is known to occur in a closed vessel freed as far as possible from radioactive air, even after due allowance is made for such gamma radiation from the soil as may penetrate the walls of the vessel. For reasons, the details of which I need not enter into, it has been supposed that this radiation is a form of gamma radiation, but of a type much more penetrating than the radiation ordinarily observed from radium. Now gamma rays possess the power of ionizing, *i.e.*, of ejecting electrons from a gas through which they pass, and the nature of their action is such that the ejected electron is sent out almost entirely in the direction of the gamma rays.

We may thus expect that such a radiation coming from above will eject electrons from the air, and these will travel certain distances in a downward direction before coming to rest. Those electrons which are shot out within striking distance of the earth will reach it and charge it. Their places will be taken by other electrons, which have been shot out from layers above, and become absorbed before reaching the earth. One advantage possessed by this type of corpuscular theory is that it invokes, for the production of the corpuscles, an agency which is already recognized for other reasons, and another advantage lies in the fact that no artificial adjustments of the theory are necessary in order to pro-



vide for a conduction current which is practically independent of altitude. With increase of altitude, the emission of corpuscles per c.c. will be reduced, but the distances from which corpuscles come will be correspondingly increased, so that if the intensity of the penetrating radiation itself remains independent of altitude, the corpuscular current will also remain independent of altitude.

Further, on submitting the theory to calculation, we arrive at magnitudes for the quantities involved which are by no means unreasonable. Thus, if we assume that only 3 high-speed corpuscles are emitted per c.c. per second, a number comparable with that which the penetrating radiation is supposed to eject, it is only necessary to assume that these corpuscles have a range of 9 metres in air in order to account for the replenishment of the earth's charge.<sup>5</sup> We shall presently see that, for reasons concerned with the ionization which would be produced by the corpuscles, it is desirable to endow them with a range greater than 9 metres; but, for the mere requirements of the replenishment of the earth's charge, an average range of 9 metres is sufficient.

*Objections to Corpuscular Theories.*—I now turn to the two main objections which may be raised against all forms of corpuscular theories. The first of these comes from failure to detect any charging effect on an insulated body exposed to the corpuscles. If corpuscles are being shot into the earth from above, an insulated mass of metal should gradually acquire a charge from the corpuscles which enter it, unless, indeed, the corpuscles are so penetrating as to pass right through it. A fairly thick mass of metal is necessary if the test is to be of value, since corpuscles which have passed through the earth's atmosphere, the equivalent of 76 cm. of mercury, will not show very much absorption in passing through a few additional centimetres of metal. I tried an experiment of this kind in 1915, but failed to find any charging effect of the type sought. More recently, von Schweidler has sought such a charging effect without success. I have always felt that my own experiments, which were done with a copper bar about 25 centimetres long and 5 centimetres in diameter, placed

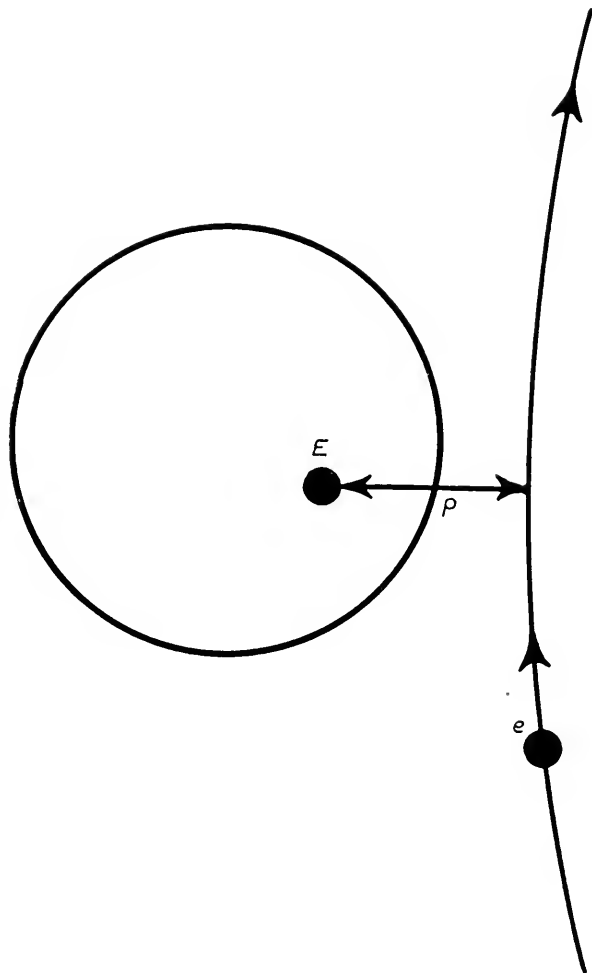
---

<sup>5</sup> A theory identical with that here given was developed, quite independently, by von Schweidler, somewhat later than the writer's original publication.



vertically, should be repeated with a larger mass of metal, and Schweidler's experiments were done with a still smaller mass of metal. However, if we should find that a sphere of metal, let us say a metre in diameter, would experience no charging effect, any theory which attributes the replenishment of the charge to influx of corpuscles would be faced with serious difficulty.

FIG. 3.



The difficulty is not insurmountable, however, if one adopts the last of the views to which I have referred, in which the ejection of the corpuscles from the molecules of air is brought about by exceptionally hard gamma rays from above. For, on this view, if the *gamma rays* are sufficiently penetrating to pass right through the metal, they will eject corpuscles from the bottom of the mass as well as inject them at the top. A simple calculation



shows that, provided the intensity of the gamma radiation does not alter in passing through the metal, all that is necessary in order to conclude that as many electrons would be shot out of the bottom of the mass as were shot in at the top, is the assumption that the ratio of the numbers of corpuscles shot out per c.c. of air and metal is equal to the ratio of the densities of these substances, and that the average ranges of a corpuscle, in air, and in the metal, are in the inverse ratio of the densities. Both assumptions are entirely consistent with our knowledge of the laws pertaining to the action of gamma rays and the passage of corpuscles through matter.

The second great objection, and perhaps the most serious objection, at first sight, to any corpuscular theory, is the fact that we might expect the passage of high-speed corpuscles through the atmosphere, on their way to the earth, to be accompanied by a much greater ionization than is observed. The situation is this: The corpuscular current necessary to balance the atmospheric electric current amounts to an influx of 1500 corpuscles per square centimetre per second. Now we know that an electron approximating in velocity to that of light produces about 40 ions per centimetre of its path, so that, in each cubic centimetre, we might expect ions to be produced to the extent of about 60,000 per c.c. per second, whereas experiment shows that they are only produced to the extent of one-ten-thousandth of this amount. In order to see how we may escape this difficulty, it may be of interest to probe a little more closely the mechanism of the ionization.

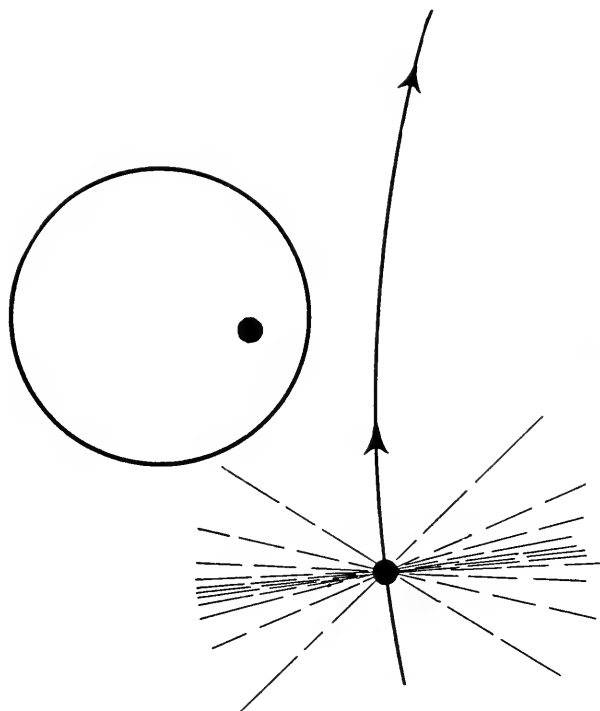
*Absence of Ionization by Corpuscles with Velocities Approimating That of Light.*—Suppose  $E$ , Fig. 3, is an electron in an atom, and that another electron  $e$ , which I shall distinguish by calling it a corpuscle, approaches the atom. The corpuscle will start to repel the electron as it approaches, and will continue to do so as it recedes, with the result that the electron receives energy, the momentum which it acquires being more or less in a direction perpendicular to the line of flight of the corpuscle. The greater the velocity of the corpuscle, the shorter the time during which the electron has opportunity to receive momentum from it. The efficiency of the corpuscle as regards its power to hurl the electron out of the atom thus diminishes with increase of its velocity, and would, as a matter of fact, become zero if the corpuscle could attain an infinite velocity. The velocity of the corpuscle cannot



attain a value greater than that of light, however, and, as regards the above effect, there is not very much reduction in ionizing efficiency for an increase of velocity from, say, 95 per cent. of that of light, where the ionization has been measured, to the velocity of light itself.

As the velocity of light is approached, however, another phenomenon comes in. The field of the corpuscle does not remain uniformly distributed. According to known electromagnetic laws,

FIG. 4.



its lines of force close up more and more into its equatorial plane, as indicated by the broken lines in Fig. 4. The time which the corpuscle has for acting effectively on the electron is therefore reduced still further on this account; but, the intensity of the action during that time is increased; and, it turns out, as has been shown by Bohr, that, if we take nothing else into consideration, the energy communicated to the electron by the passage of the corpuscle will be unaffected by this concentration of the lines of force.

There is one other very important consideration which we must take into account, however. If an electron receives even a small velocity in a very short time it is known that it will radiate



a large amount of energy. Its sudden start results in a violent jerk in the æther. On submitting this matter to calculation it turns out that, even if we should wish to give to an electron but a small amount of energy, in an infinitesimal time, it would be necessary to pay a sort of tax, of an infinite amount of energy, in the shape of radiation. Now the more nearly the corpuscle approaches the velocity of light, the more suddenly does it communicate to the electron such energy as it imparts. Without entering too greatly into details, we may describe the situation as follows: In the case of a corpuscle moving with a velocity approximating that of light (say 95 per cent. of the velocity of light), but not so closely as to involve these radiation considerations, it turns out that the corpuscle must approach an electron of an oxygen atom within  $0.7 \times 10^{-10}$  cm., in order that it shall be able to eject that electron from the atom. Now it is possible to assign to the corpuscle a velocity so nearly equal to that of light that, if it should pass the electron at  $0.7 \times 10^{-10}$  cm., the radiation tax alone, accompanying ejection of the electron, would amount to more energy than could be imparted by the corpuscle; and, the conditions are such that the situation is still more unfavorable for ejecting the electron if the corpuscle comes nearer to it than  $0.7 \times 10^{-10}$  cm. It is quite true that, in the absence of the radiation forces, the electron would receive more energy the nearer the distance of approach, but with radiation taken into account, the electron when approached within  $0.7 \times 10^{-10}$  cm. by a corpuscle of sufficiently high speed is in the position of a man whose salary is so large that if he took it, his income tax would be greater than his salary, on account of the very large tax on high salaries, so that he would get more if he had a smaller salary. The electromagnetic equations are kind to the electron, however, and allow it to refuse its salary under these circumstances. The net result of all this is that, if the velocity of the corpuscle is sufficiently high, it will be unable to eject the electron if it passes at a distance of  $0.7 \times 10^{-6}$  cm. It will be unable to eject it if it approaches nearer than this, on account of the radiation reaction. But, it would be unable to eject it on passing at a distance greater than this if the radiation considerations were absent. The result is that it cannot eject the electron at all. In submitting the matter to calculation, we find that a corpuscle with a velocity 200 metres per second



less than that of light would certainly be unable to eject an electron from an atom of nitrogen, or oxygen.<sup>6</sup>

It may be of interest to observe that, if we are to suppose that corpuscles come to the earth from outside the atmosphere then, quite apart from all question of absorption in the atmosphere, it is necessary to assume a certain minimum velocity in order to account for their getting here, at least in the vicinity of the equator. For the path of a moving corpuscle is bent by a magnetic field, and it may be bent so much as to cause the corpuscle's return into space. The more nearly a corpuscle approaches the velocity of light, the less is its path bent. The diminution of bending is not so much a direct consequence of the greater speed as it is of the greater mass which results from greater speed. It turns out that, in order that a corpuscle injected into our atmosphere in the vicinity of the equator should be able to reach the surface of the earth without being turned back by the earth's magnetic field, it would have to possess a velocity which is too great to permit it to ionize the air through which it passes.

Birkeland has endeavored to account for the main features of the aurora by supposing it to be produced by the entry into our

---

<sup>6</sup> Without invoking these considerations, and utilizing only the older views, von Schweidler (*Akad. Wiss. Wien Ber.*, 1918, 127, 2a, pp. 515-533) has concluded that the ionization per centimetre of path should diminish indefinitely as the corpuscle approaches the velocity of light. It would appear, however, that this argument cannot be substantiated. It is based on the fact that the older theories give the ionization per centimetre of path as inversely proportional to  $mV^2$ , where  $m$  is the mass, and  $V$  the velocity of the corpuscle. For slow velocities,  $\frac{1}{2}mV^2$  is the kinetic energy, so that the statement is made that the ionization per centimetre of path is inversely proportional to the kinetic energy. Von Schweidler, taking this statement, substitutes for  $\frac{1}{2}mV^2$ , the relativity expression for the kinetic energy, which becomes infinite when  $V$  approaches the velocity of light, and thus concludes that the ionization per centimetre of path should diminish indefinitely as that limit is attained. It is to be observed, however, that  $\frac{1}{2}mV^2$  occurs in the original expression for the ionization per centimetre of path not because it is the kinetic energy. The occurrence of  $V^2$  in the denominator of that expression is closely bound up with the fact that the time during which the corpuscle is in effective proximity to the atom diminishes with increase of velocity. In fact, this quantity  $V^2$  is not the representative of something which should really become infinite when  $V$  attains the velocity of light, as a detailed examination of the elements involved in the calculation of the ionization per centimetre of path will clearly show.



atmosphere of high-speed corpuscles from the sun. In order to account for the facts as regards the bending which the paths of these corpuscles should suffer in the earth's magnetic field, he is forced to assume velocities ranging from 400 metres per second less than the velocity of light to 4 metres per second less than that limit, so that the velocity at which ionization should cease falls well within the limits assigned by Birkeland. It is quite true that the present theory leads to the conclusion that Birkeland's corpuscles would not ionize at all, so that they could not well account for the aurora; but, it is now generally believed that the aurora is not caused by the ionization produced by negative electrons, and I only cite this connection with Birkeland's calculations to show that, in invoking speeds only 200 metres per second less than that of light, we are not doing anything more drastic than has been done already in other branches of the subject.

It may be remarked, moreover, that if we extrapolate Bohr's theory of absorption to velocities comparable with 200 metres per second less than that of light, we find that corpuscles having this velocity could pass through distances in the atmosphere comparable with a kilometre. When we recall that transfer of energy to electrons in the atoms constitutes the process by which the corpuscles lose energy on Bohr's theory, we see that the reduction in this transfer, symbolized by failure to ionize, will still further increase the possible range. Thus, the nature of all the considerations involved is such as to result in mutual consistency in the views that if corpuscles should enter our atmosphere with speeds sufficiently near that of light to enable them to reach the earth's surface in the vicinity of the equator, without being turned back by the earth's magnetic field, they would pass right through the atmosphere with limited absorption, and would fail to ionize the air through which they passed.

It would thus appear that the difficulties attending the ionization which might be expected to follow, at first sight, from any corpuscular theory of the earth's charge are not unsurmountable. But while, as regards the mere replenishment of the earth's charge, we could avoid the assumption of long ranges, as in the theory which invokes the penetrating radiation to eject the corpuscles from the air, we have to postulate, for the corpuscles, velocities



closely approximating that of light, in order to explain the absence of ionization, and this in itself implies long range as a consequence.

Attempts have been made to overcome the supposed difficulty attending the absence of any charging effect in the case of an insulated body by supposing the influx of corpuscles to take place in the auroral belt. It is perhaps worth while pointing out that, even should we do this, we could not escape the difficulty attending the ionization by these particles, unless we adopt some such theory as I have sketched; for, if we assume the ordinary ionization per centimetre of path, it becomes necessary to invoke recombination, to cut down the resulting ionic density, to such an extent that we must suppose the area of precipitation to be less than one-thousandth of the area of the earth, as otherwise the conductivity produced in the air would be so great that, for a potential gradient of 150 volts per metre, we should calculate, for this region alone, a total conduction current greater than the corpuscular current.

#### THE ORIGIN OF THE EARTH'S MAGNETISM.

The fact that the earth possesses the power of controlling the direction in which a magnetic needle points was known to the ancients. The earth acts, in fact, approximately as though it were a huge magnet with two poles, one in the vicinity of the north geographical pole, and the other in the vicinity of the south geographical pole. The problem of accounting for this condition of affairs has been one of the most fascinating fields for speculation in cosmical physics.

Of course we may say that the interior of the earth contains, in a large degree, a magnetizable material like iron, and that it got magnetized somehow or other, at some time or other, and that is the end of it. We cannot shuffle off responsibility for an explanation quite so easily, however; for, we know that if we heat a steel magnet to a temperature of 785 degrees centigrade it loses its magnetism, and we have reason to believe that temperatures considerably higher than this are attained within the earth. We can escape this conclusion provided that we are willing to suppose that the great pressures inside the earth raise the temperature at which magnetism is lost; but, until further evidence upon the effect of pressure in this respect is available, one is tempted to seek some



more fundamental cause as responsible for the earth's magnetic state.

It is hard to resist the temptation, which has been felt by many, to suppose that the earth's magnetism is bound up in some way with its rotation. It is true that most simple theories based on this view lead to a state of magnetization symmetrical with the geographic axis, and do not, moreover, spontaneously suggest that remarkable characteristic of the earth's magnetism exemplified in its secular variation. Nevertheless, one might feel well satisfied with his progress if he could see any reasonable way in which a body like the earth could acquire magnetization of any kind comparable in amount with the earth's magnetization.

*Theories Involving Rotation of Electrostatically Charged Systems.*—We know that an electric current flowing in a circular wire gives rise to a magnetic field; and, if we were to wind the surface of a sphere with a single layer of coils, and then pass a current through the coils, we should obtain a magnetic field approximating in type to the earth's field. Now since the earth is electrically charged, the first idea which might occur to us is to see whether the current formed by the rotation of this charge with the earth will give an appreciable field. The charge density is known, and the velocity of the earth's rotation is known, so that it is a comparatively easy matter to compute the effect. Neglecting the effect of the positive charge in the atmosphere, we find that the magnetic field produced amounts to only the one-hundred-millionth part of the earth's field. In so far as the earth's charge produces a very considerable electric field at its surface, we see that a charge density necessary to give a magnetic field comparable with the earth's field would give rise to an electric field almost inconceivably large. Moreover, it is well known that, on account of the effect of the motion of the observer with the earth's surface, the field would appear to him different from the field which would be observed by a stationary observer, and the nature of this effect of the observer's motion is such as to cause the vertical component of the field to have the wrong sign if the sign of the charge is adjusted to give the correct sign for the horizontal component.

When we take the motion of the atmospheric charge into account, the result obtained is still more curious. To a stationary



observer, the vertical component is now zero everywhere,<sup>7</sup> while to an observer participating in the earth's motion, both the vertical and the horizontal components are zero.

There is, however, another way in which we may obtain a magnetic field by the rotation of charges, without the necessity of imagining any external electric field. If we imagine a sphere of positive electricity and set it in rotation, it will give rise to a magnetic field; but, for a given total charge, the strength of the equivalent magnet will be greater the greater the diameter of the sphere. Thus, if we superpose two spheres of slightly different sizes, one sphere being made of positive, and the other of negative electricity, but each containing the same total charge, they will act as oppositely directed magnets of different strengths, and there will be a residual magnetic effect. As far as the electric field is concerned, however, there will be no residual effect at points external to the sphere. Now, modern physics tends to the belief that all matter is composed of nothing but positive and negative electricity; and, it appears that, while a cubic centimetre of, say, iron is neutral as a whole, nevertheless, the amounts of positive and negative electricity in it are so great that if we could separate them and concentrate them in two points one centimetre apart, they would attract each other with a force equivalent to  $10^{20}$  tons. In view of this very large amount of the electricity of each sign present, it turns out that we may account for a magnetic field comparable with the earth's field, if we are willing to suppose that the positive electricity in the earth is distributed throughout a sphere which is less in radius than the sphere of negative by only  $2 \times 10^{-8}$  cm.,

---

<sup>7</sup> At first sight, this statement seems to be inconsistent with the fact that the tubes of magnetic induction from closed curves, since they are apparently prevented from escaping through the positive layer, or into the earth, on account of the absence of a vertical component. The point is that, owing to the thinness of the positive layer, the volume of the space between the earth's surface and a sphere within which practically all the positive charge lies is relatively small. The total magnetic flux across any annular section of this space is small, so that a practically infinitesimal vertical component is all that is necessary to permit of the entry and exit of the lines of magnetic induction to and from the space, since the area available for such entry and exit is the whole area of the earth's surface. Indeed, that there is nothing fundamentally mysterious in the nature of the field here cited will be recognized when it is pointed out that it is simply the field obtained by superposing on the field due to a uniformly magnetized sphere, a uniform field parallel to the axis of magnetization.



*i.e.*, we need only imagine the diameters of the two spheres to differ by as much as that of a single molecule.

However, in spite of the very strong temptation to lean to this view, which was first considered by Sutherland, we are confronted with a very serious difficulty when we come to seek an explanation of why the positive and negative can remain separated by even this small amount; for calculation shows that, at the surface of transition, there would be an electric field of one thousand million volts per centimetre protesting against this separating of the charges.

There are a number of causes which would operate in some degree towards producing separation of charges such as would give rise to a magnetic field as a result of the earth's rotation. Thus, it is customary to suppose that, in a solid, a large proportion of the electrons are not bound in the atoms but are free to roam about in the interstices between the molecules in very much the same way as the molecules of air fly about between the leaves of a tree. Owing to the centrifugal force of the earth's rotation, these electrons will tend to be thrown outwards. This tendency will be resisted by the attraction of the positive electricity which they would leave behind. Still there will be a small tendency in this direction; and, as a result of the rotation of this system in which the charges have been displaced, we should obtain a magnetic field. However, on submitting the matter to calculation, it turns out that the field so obtainable amounts to only  $10^{-23}$  of the earth's magnetic field, and is, moreover, of a type differing widely from it.

Again, owing to the earth's gravitation, the electrons will tend to move towards the centre. Apart from sign, this leads to the type of displacement postulated in Sutherland's theory; but, when we work out the magnetic field, we find that it amounts to only  $10^{-21}$  of the earth's field, and is, moreover, in the wrong direction.

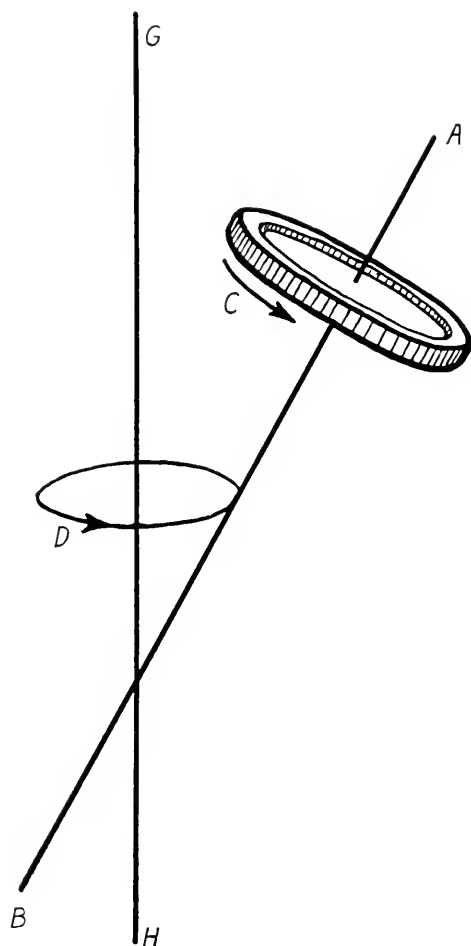
I may refer to still another possibility. We know that the inside of the earth is hotter than the outside. Now if we have a temperature gradient in a gas, the gas will become less dense where the temperature is high than where it is low, so the electrons will tend to become less dense in the hot regions than in the colder, this tendency being resisted by the electrostatic attraction which is set up as a result of the separation. On working this case out, we find that the magnetic field resulting from it amounts to



only  $10^{-17}$  of the earth's field, although it happens to be in the right direction.

There are a number of other possibilities somewhat similar to those which I have discussed; but, on submitting them to calculation, they all lead to fields of an order of magnitude quite infinitesimal compared with the earth's field. I think we may con-

FIG. 5.



clude, as a general rule, that it is practically hopeless to seek an explanation of the earth's magnetism on the basis of the rotation of charges which have been separated against electrostatic attraction, since the mechanical forces necessary to produce the required separation must be, in all cases, enormous.

*Theories Involving Gyroscopic Action.*—Let me now turn to another possibility. We know that the molecules of iron tend to act like little magnets, and the magnetization of a steel bar consists in the process of partially orienting these little magnets so



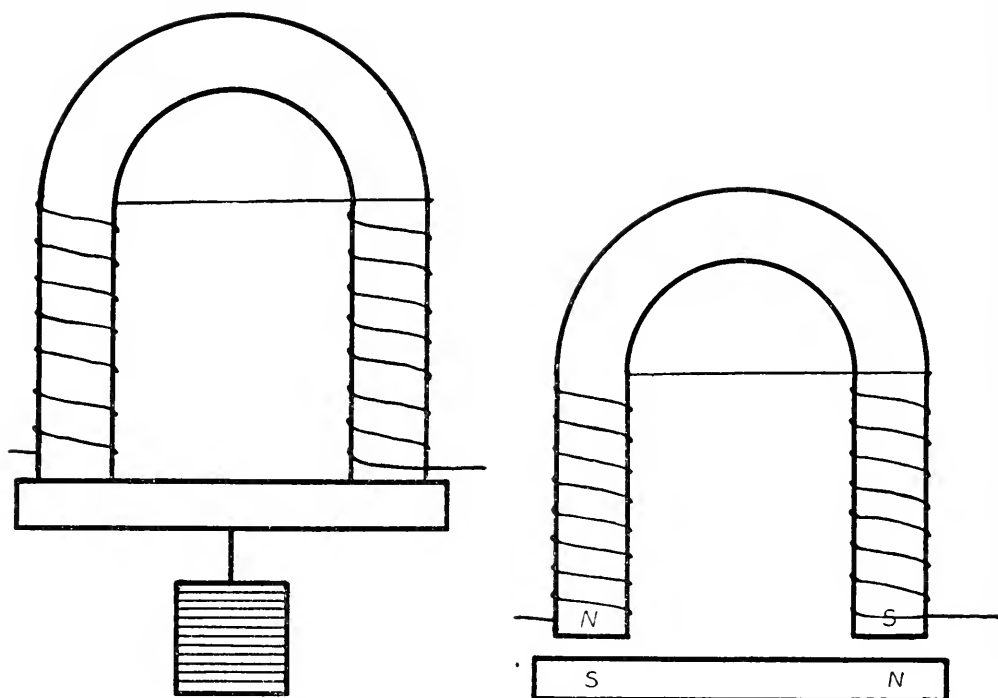
as to point more or less in one direction. Now a circular hoop of wire carrying a current acts like a magnet with its axis perpendicular to the plane of the hoop; and it is generally supposed that an atom receives its magnetic character on account of the circulation of electrons within it. This circulation of electrons makes the atom act like a gyroscope. Now it is well known that, if a gyroscope be set in rotation about its axis  $AB$ , Fig. 5, in the direction indicated by the arrow  $C$ , for example, and if this axis is then caused to rotate about another axis  $GH$  in the direction indicated by the arrow  $D$ , it will tend to turn parallel to  $GH$ . If, therefore, the earth is composed largely of iron, there will be a tendency for its molecular magnets to turn their axes parallel to the axis of rotation. That a piece of iron may be magnetized by rotation has been experimentally demonstrated by S. J. Barnett; but, when we come to apply these results to the earth, we find that it is not possible to account, by this means, for a magnetic field larger than about  $2 \times 10^{-10}$  of the earth's field.

It is well known that different substances may be magnetized to different degrees by the same magnetizing force. Easily magnetizable substances are said to have a high permeability. The suggestion has been made that, on account of high pressure, or some other cause, the interior of the earth may possess an enormously high permeability, and that, in consequence, a very weak magnetizing force, such as that arising from gyroscopic action, may be sufficient to endow it with appreciable magnetization. Such a view must, however, meet a very serious objection, which I can illustrate by calling your attention to a well-known experiment. If a horse-shoe electromagnet be excited by an electric current and caused to hold up, say, a 100-pound weight attached to its armature, it will be found that the weight will continue to be held after the current is stopped, provided that the pole faces, and the armature, are truly plane. The complete iron circuit composed of horse-shoe and armature having been magnetically excited, remains so after the stoppage of the current. If now the armature be forcibly removed from the horse-shoe, magnetic poles appear at the points of separation, as indicated in Fig. 6. The action of these magnetic poles is such as to destroy the state of magnetization previously existing in the horse-shoe and armature, and, as a result, it is found that now, not only will the horse-shoe refuse to support the armature and 100-pound weight, but it will even refuse to support



the armature alone. It is much more difficult to magnetize a short piece of iron than a long one, on account of the proximity of the poles to the main body of the iron in the former case. In fact, these poles produce, within the iron, a magnetic field which is in such a direction as to tend to demagnetize it. In the case of a magnetized sphere, the effect of the poles is to produce within the body of the iron, a demagnetizing field equal to the field which the sphere itself produces at an external point on its equator. Hence, any primary magnetizing agent which is to be ultimately responsi-

FIG. 6.



ble for the production of the earth's field by orientation of the molecular magnets, must be of such intensity that it will produce, on the molecular magnets, forces at least equal to the forces which would be produced on them by a magnetic field equal in intensity to the earth's magnetic field at the equator.

*Theories Involving the Circulation of Currents Within the Earth.*—The earth's field could be accounted for if we could account for a suitable circulation of currents in the earth's interior. Such an attempt at explanation immediately calls, however, for an explanation of the electromotive forces wherewith to sustain the currents. In this connection, it is not without interest to recall



a calculation made by H. Lamb, many years ago, the significance of which I shall endeavor to explain.

If we start a current in a wire, and then leave it to itself, it will die to zero almost immediately on account of the resistance offered by the wire. The situation is analogous to what we should have were we to take a hollow anchor ring, fill it with water, and then give it a sudden rotation. If there were no friction, the water would go on swirling around for ever; but, on account of the friction, it is soon brought to rest. If the water were less dense, and had therefore less inertia, it would be brought to rest sooner. The analogy between the motion of the water and that of electricity is not very close, but the electric current does possess the property of inertia, and it turns out that the inertia of a current is greater in a large hoop than in a small one. So important does this inertia become when dealing with a body of the size of the earth that, as Lamb has shown, if a system of currents were started in a sphere of the earth's size, having a conductivity equal to that of copper, and if the electromotive forces which were responsible for starting them were removed, it would take about ten million years for the currents to decay to one-third of their original values. Attempts to account for the earth's field in this way have met criticism on the basis of the enormous currents which would be calculated by extrapolating back, even to epochs not more remote than those during which the earth's crust has been solid, so that, unless there is some reason for supposing that the conductivity is, or has been in the past, even greater than that of copper, we are confronted with the necessity of accounting for enormous amounts of energy necessary to have produced the magnetic field originally.

The actual current density within the earth, necessary to account for the earth's field, is very small, being, for example, only the one-hundred-millionth of an ampere per square centimetre on the surface at the equator, for the case where the current density is proportional to the distance from the axis of rotation. I have already referred to the largeness of the amounts of positive and negative electricity in a cubic centimetre of the earth. If, taking a sphere of iron of the size of the earth, we assume that there are about  $10^{23}$  free electrons per cubic centimetre, a not unreasonable number, we find that it is only necessary to suppose that the electrons at the earth's surface differ in velocity from the matter in which they reside by one part in  $7 \times 10^{16}$  of the velocity of that



matter in order to account for a current of one-hundred-millionth of an ampere. It is perhaps not too much to hope that a fuller knowledge of the mechanism of conduction of electricity in solids than we have at present may lead to an explanation of such a small difference as arising directly on account of the earth's rotation. It may not be a question of accounting for an electromotive force wherewith to overcome the electrical resistance of the material of the earth, but rather of showing that, in a rotating body, the condition of electronic motion which is permanent, the motion which must exist in order that there shall be no further degradation of energy into heat, is one in which there is a finite relative motion between the free electrons and the substance of the rotating body.

A small relative velocity between the free electrons and the substance of the earth may be accounted for on ordinary lines if we assume that the velocity of the earth is diminishing on account of tidal action. If the retarding forces operated on the earth and not on the free electrons the latter would tend to retain their angular velocity undiminished. As a matter of fact, they would actually lag behind the remainder of the matter to such an extent that the force brought into play upon them, on account of this lag, a force calculable in terms of the specific electrical resistance, was just sufficient to cause them to follow the earth in its retardation. However, on submitting this matter to calculation, it appears that the earth would have to be retarded at such a rate as to lose the whole of its velocity in less than one day if the current thus produced were to be sufficient to account for the earth's field.

We can account for a small magnetic field if we suppose that, while the negative electrons participate in the translatory motion of the matter in which they are contained, they do not rotate with reference to axes fixed in space. The effect in such a case is, in fact, to give rise to a magnetic field which is the net equivalent of what we should have if everything were stationary except that each electron rotated in a direction opposite to that of the earth, about an axis in itself, once per day. The magnetic field produced in this case amounts to only  $1.6 \times 10^{-25}$  of the earth's field and is moreover in the wrong direction. It may be of interest to observe, however, as a mere matter of numerical interest, without any implication of a bearing on the earth's magnetism, that if we could divide all of the positive electricity in the earth into groups about a centimetre in average radius, and then see some way by



which these little groups could go around with the earth without rotating, while all the negative electricity participated in the rotation as well as the translation, we should have a way of accounting for a magnetic field of the order of magnitude of the earth's field.

*Possibilities Inherent in a Slight Modification of the Fundamental Laws of Electrodynamics.*—There is always the chance that the origin of the earth's magnetism may have to be sought in some fundamental but small departure from the ordinary laws of electrodynamics. In this connection, I would remind you of a somewhat analogous modification which was suggested by H. A. Lorentz, to account for gravitation. Lorentz showed that if we should imagine that the attraction between a positive and a negative electron exceeded the repulsion between two positive or two negative electrons, by one part in  $3 \times 10^{36}$ , the residual attraction would be sufficient to account for gravitation. After paying all due regard to the care necessary in defining what we mean by a neutral body in such a case as this, Lorentz's theory may be shown to lead to the conclusion that, in order that the free electrons in a body may be in equilibrium, the body must acquire a charge density to an extent not wholly determined by the weight of the electrons. Schuster has discussed the possibilities in this connection; but it would appear that, under the most favorable assumptions, the density would be insignificant as regards producing, by its rotation, a magnetic field comparable with the earth's field.

A rather greater measure of success is attained by making a somewhat similar assumption with regard to the magnetic field produced by a moving charge. I will remind you of the fact that, when a charge is in motion in a magnetic field, it experiences a force in a direction perpendicular to the plane containing the direction of its velocity and the direction of the magnetic field. It is of course, this force which is responsible for the operation of the electric motor. Even when we measure a magnetic field in terms of its action upon a magnet, it is this force which is really at the basis of the action, since the magnet derives its properties from the electrons revolving within it. In analogy with the case of electrostatics, where we have to deal with the forces produced by positive on positive, negative on negative, and positive on negative, we have in addition, for moving electrons, the force due to the motion of a positive electron on a moving positive electron, the



force due to the motion of a moving negative electron on a moving negative electron, the force due to the motion of a negative electron on a moving positive electron, and the force due to the motion of a positive electron on a moving negative electron.<sup>8</sup> If, for similar motions, these four forces are all equal, a moving electron, or a magnet, would be entirely unaffected by the rotation of the earth as a whole. If, however, the forces, due to motion, between unlike moving charges are suitably different from those between like charges in the same states of motion, it will immediately appear that the electrically neutral earth will, by its rotation, produce those forces on magnets and moving electrons which we associate with a magnet as ordinarily defined. By making the forces between electrons of like sign equal for both signs, the force due to the motion of a negative electron on a moving positive electron greater than, and the force due to the motion of a positive electron on a moving negative electron less than the forces between like electrons to the extent of about two parts in  $10^{16}$ , we can account for the equivalent of a magnetic field of the order of magnitude of the earth's magnetic field.<sup>9</sup> If we wish to combine these alterations with suitable alterations in the electrostatic forces, we can also include gravitation in the complete scheme.

*The Bearing of the Secular Variation.*—There is some evidence to support the belief that the earth's magnetic axis rotates about the geographic axis once in about 500 years. Now we know that if, by any means, we cause the number of lines of magnetic induction passing through any area of a conductor to change, induced currents will be set up in the conductor. This is merely another aspect of the inertia associated with electromagnetic phenomena, to which I have already referred. The movement of the earth's magnetic axis within the earth itself will therefore give rise to induced currents, and the magnetic field which we observe will be that due to these induced currents (the secondary field), and that due to the primary causes (the primary field). Taking an iron sphere of the size of the earth for purposes of illustration, it turns out that the flux of magnetic lines of induction of the secondary field through

<sup>8</sup> The first two of these may serve as the means of defining the magnetic fields due to motions of positive and negative electricity respectively since, on the present lines, each of these needs independent definition.

<sup>9</sup> Incidentally it may be remarked that it is possible to make the modification of the law in a form consistent with the restricted theory of relativity.



the sphere, which flux is of course related to the primary field, is of such a magnitude as to almost completely annul that component of the primary flux which is perpendicular to the axis of rotation. As a result, there is left only a small residual non-axial component. Thus, in order that the resultant flux shall have an appreciable inclination to the geographic axis, it is necessary for the primary axis to lie very near to the equatorial plane, and yet for the primary flux to be so large that its axial component which is small compared with it, represents the axial component which we observe. This practical coincidence of the primary axis of magnetization with the equatorial plane would be, of course, very remarkable were it true. The considerations involved in deducing it involve the assumption of an electrical conductivity comparable with that of iron; and, while it is not implied that the main body of the earth has a conductivity of this order of magnitude, it may nevertheless be of interest to call attention to the curious results which would follow from the secular variation if it had.

*The Diurnal Variation.*—The magnitudes of the earth's magnetic elements go through fairly regular variations throughout the day and throughout the year; and, we are in a much better position for an explanation of these than we are for the explanation of the earth's field as a whole.

When a conductor moves across the lines of force of a magnetic field, currents are induced in it, this being, of course, the principle at the basis of the operation of the dynamo. Now the air is continually in motion under tidal action, just as the sea is in motion; and, as it moves it cuts across the earth's lines of magnetic force. Electromotive forces are consequently produced in the atmosphere; and, these give rise to currents to an extent determined by the conductivity of the atmosphere. The currents result in magnetic fields, and these magnetic fields, being thus related to the atmospheric tides, may therefore be expected to experience diurnal and seasonal variations. Such was the suggestion originally made by Balfour Stewart, and subsequently worked out in detail by Schuster.

It will be observed that the magnitudes of the effects to be expected depend upon the conductivity to be assigned to the atmosphere. The lower atmosphere is so poor a conductor that its effect in contributing anything to the phenomenon is negligibly small. There are, however, reasons for believing that the conductivity of



the upper atmosphere is very much greater ; and, for certain reasons into which I need not enter, Schuster has supposed that appreciable conductivity may be considered as confined to a layer of the atmosphere 300 kilometres thick, situated at an altitude where the average pressure is one-millionth of an atmosphere. The conductivity which he finds necessary to account for the phenomena is, however, three hundred thousand million times as great as the conductivity at the earth's surface. To realize what this means it may be remarked that, with such a conductivity, a column of air extending completely round the earth, in the upper atmosphere, would have a resistance no greater than that of a column of equal cross-section and only one-thirtieth of a centimetre long, at the earth's surface. In other words, such an assumption means, to all intents and purposes, that the earth may be supposed to be surrounded by a conducting shell. Startling as this assumption may seem, it falls in well with the requirements of other phenomena. Thus, in discussing the origin of the earth's charge, we had occasion to consider the possibility of the existence of such a layer. Again, it has been for long a matter of contention as to why wireless waves travel such great distances over the earth's surface. On elementary considerations we should suppose that their energy would be dissipated into space, and that very little would succeed in travelling far around the earth. On the other hand, the conducting shell provides us with a way out of the difficulty. For, such a shell would reflect the waves in a manner analogous to that met with in the case of sound waves transmitted round a whispering gallery, or through a speaking tube. Of course the same considerations would apply to show that wireless waves coming from the outside would fail to get inside the conducting shell, for they would be reflected at its surface. We must not apply this argument with too great generality, however, for light is really an electromagnetic disturbance of very short wave-length, a sort of very short wireless wave ; and, it would be unfortunate for the theory were it to show that light cannot come through the shell.

It is probable that the ultra-violet light plays no important rôle, as it is capable of accounting for a conductivity less than one-millionth of the conductivity required. Other agencies which are frequently invoked to account for the conductivity are corpuscular radiations from the sun. Some radiation of this kind seems necessary to account for the aurora.



*The Aurora.*—Auroral displays take varied forms, and are of varied hues and colors, but they are confined mainly to high latitudes. A characteristic feature of the aurora is the sharp boundary at its lower edge. The height of this boundary has been measured by various observers, and appears to vary from 70 to 300 kilometres with a maximum number at about 115 kilometres. Auroral activity is confined largely to two zones of the atmosphere situated at an angle of about 20 degrees to the polar axis. One of the best-known theories of the aurora is that which attributes it to light caused by the ionization of our atmosphere, by negative electrons emitted from the sun. We know, from laboratory experiments, that beams of swiftly moving charged particles are deflected by a magnetic field; and, Birkeland, on the experimental side, and Störmer, on the mathematical side, have done much work with the object of finding out how far the characteristics of the aurora can be accounted for on the view that it is caused by a stream of negatively charged particles which come from the sun, and are precipitated into our atmosphere under the bending action of the earth's magnetic field. The two zones of active precipitation become satisfactorily accounted for, except that they occur at latitudes higher than those corresponding to observation. The cause of the difficulty is the small mass of the electron, which results in too large a bending of the paths by the earth's magnetic field. Now, as I have remarked earlier in this paper, the mass of a corpuscle increases with its velocity, and becomes theoretically infinite for a velocity equal to that of light; but, to such an extent has Birkeland found it necessary to draw upon this fact, that he must suppose the corpuscles responsible for the aurora to have velocities ranging between 400 metres per second less than that of light and 4 metres per second less than that limit, in order to make the theory fit the facts.

In order to overcome the difficulty inherent in the small mass of the electron, Vegard and others have supposed that the particles responsible for the aurora are not electrons, but alpha particles emitted by the sun. Alpha particles would have about the right velocity and mass to provide for the necessary bending. Moreover, the characteristic features of alpha particles are the straightness of their paths, and the very sharp limit to the range of their action. Both of these are well typified in the aurora, the straightness of the path by the straightness of the streamers, and the sharp



limit of the range by the sharp lower boundary of the luminescence. The fact that alpha particles only travel for a distance of a few centimetres in air at atmospheric pressure presents no difficulty, for the pressure in the auroral regions is very small. As a matter of fact, the range of the alpha particle is amply sufficient to account for the depth of penetration; and, in so far as there is any difficulty in this matter at all, it arises from the fact that, on certain plausible views as to the composition of the upper atmosphere, the range of ordinary alpha particles is rather too large to account for the facts.

Not only for the explanation of the aurora has the aid of alpha particles from the sun been invoked, but they have also been called in to account for those sudden perturbations of the earth's magnetic field known as magnetic storms. These perturbations are most frequent at times when the number of sun-spots is a maximum, so it is natural to attribute them to something emitted from the sun-spots.

As illustrating the difficulties confronting any explanation of these storms in terms of alpha particles, I may quote a few of the objections which have been raised by Lindemann. In order to account for the facts, it becomes necessary to suppose the particles to be shot out in a sort of cone. Now Lindemann points out that, in the first place, the magnitudes of the phenomena involved are such as to necessitate an incredibly large amount of radioactive material in the sun; in the second, the alpha particles could not remain together as a beam on their journey from the sun to the earth, on account of self-repulsion. A beam of the necessary intensity would show a lateral spreading corresponding to an acceleration of the order  $10^{13}$  cm./sec.<sup>2</sup> at its boundary. Finally, even though the alpha particles could reach the earth's atmosphere as a beam, they would charge it at such a rate that, after a few seconds, no more could come here on account of the repulsion of those which had already arrived.

Lindemann himself puts forward the view that the particles which enter the atmosphere from the sun, and are responsible for magnetic storms, and for the aurora, are really gaseous ions shot out from the solar prominences. These prominences, it will be recalled, are composed of flaming masses of gas, some of which attain the incredible heights of 300,000 miles; and their forms change so rapidly as to tell us that the gases which compose



them must move with stupendous velocity. Velocities of the order 80 million centimetres per second are not uncommon.

We know that if light falls upon a particle, a pressure is exerted upon the surface of the particle; and the smaller the particle, the more effective is the light in producing velocity therein. It will be recalled that it is customary to assume that the reason why comets' tails bend away from the sun rather than towards it, as gravitation would lead us to believe, is that the pressure of light tending to drive the particles away from the sun is, on account of their small size, more effective than gravitation which is pulling them toward it. Lindemann has consequently supposed that the huge velocities attained by the gases in the solar prominences are attained under light pressure; and he further shows that, as a consequence, some of this gas may be expected to shoot out into space with such high velocity as to give the atoms properties similar to those of alpha particles. He supposes that the gas is almost completely ionized on account of the high temperature in the prominences, so that the particles shot towards the earth are of both signs, thus securing absence of spreading due to self-repulsion.

I must not enter into the details of Lindemann's theory of the phenomena. I would point out, however, that, from various points of view, we are lead to the conclusion that high-speed corpuscles of some kind or another are shot into our atmosphere from the sun and are probably ultimately responsible for magnetic storms, for the high conductivity of the upper atmosphere, and for auroral phenomena.

It is very fortunate that our knowledge of the upper atmosphere rests practically completely upon conjectures, and that we have no direct experimental data on the electrical conditions at the altitudes concerned. If only we could get up there with some apparatus we should be much better off.

#### GRAVITATION.

It is not possible to deal adequately, with the great problem of gravitation, in a short space, and I must confine myself to but a few remarks concerning it. In seeking an explanation of such a phenomenon as gravitation it is perhaps not inappropriate to inquire how much we are justified in expecting from nature in the way of a cause. We say, or some of us say, that Newton discovered the force of gravi-

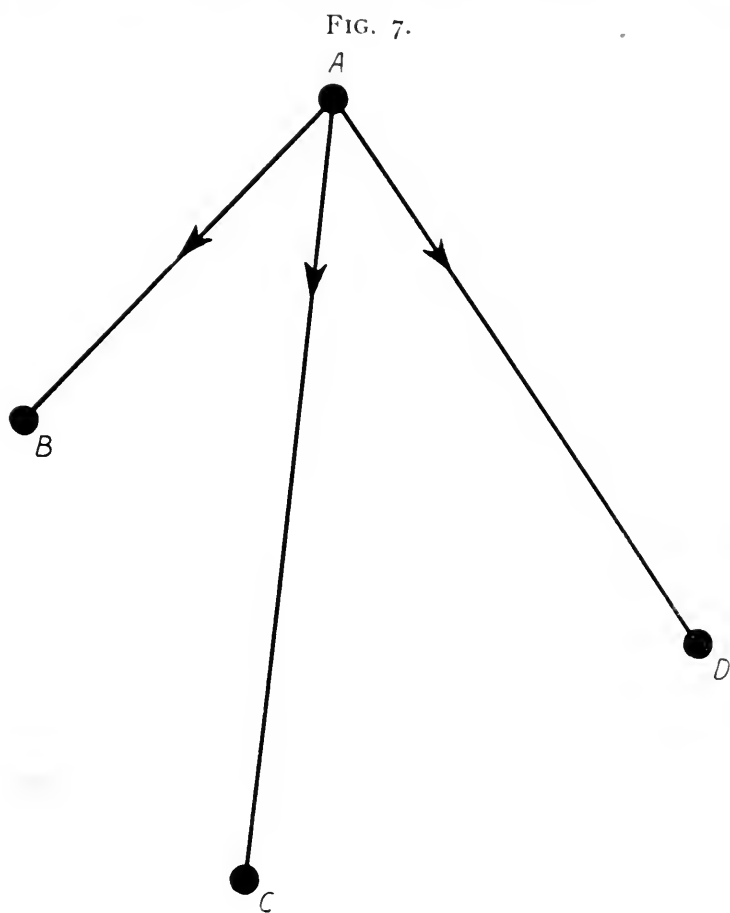


tation, and we have occupied ourselves ever since in trying to find the cause of gravitation. Now what sort of an explanation should we be content with? Well, the picture of the earth whirling around the sun without flying away from it strongly suggests to the mind the picture of a stone whirling around at the end of a piece of elastic, so we are tempted to picture some sort of elastic pull emanating from the sun. Now suppose that somebody had succeeded in accounting for gravitation in terms of the elastic properties of an intervening medium, how much comfort would we be justified in extracting from this? Shall we say, now all is clear, there is in reality not a great nothingness surrounding the sun, but a medium with elastic properties, and this medium does the pulling. If we do, some pestering philosopher may say: but, why does the elastic pull? Well, we shall answer, that is a matter of cohesion. The elastic is composed of a lot of little molecules and when these are separated from each other, they tend to return. But, says the philosopher, why do they do this? We reply, although the molecules are apparently separated from each other there is really a medium between them, and this medium is endowed with elastic properties and does the pulling. But, says the philosopher, why does the elastic pull? And so we may go on discussing the matter *ad infinitum*. We cannot in fact come to any ultimate explanation of the matter. The very best we can do is to conclude that this phenomenon of gravitation for which we cannot account, acts in many respects like that other phenomenon concerned with the elastic for which we also cannot account.

Now in the statement of Newton's law of gravitation there is really no reason to speak of force at all. What Newton found is that if, for example, a particle is moving far away from all other bodies, it moves in a straight line with constant velocity, but if two particles come into each other's vicinity they approach each other with an acceleration inversely proportional to the square of the distance between them. In general, he found that one could describe the motion of a particle *A* in this way: Join the particle to any other particle *B* in the universe. Write down, for the particle *A*, an acceleration in the line joining it to the particle *B* and proportional to the inverse square of the distance between them, and to two numbers, the masses, characteristic of each. Then draw a line to another particle *C*, and write down another acceleration, in the line adjoining *A* and *C*, and proportional to the inverse



square of the distance, and to two mass numbers characteristic of  $A$  and  $C$ . Do this for all the particles in the universe. Compound the accelerations by the usual vectorial procedure, and the result will represent the acceleration of the particle  $A$ . In this statement of the law as a mere empirical fact, we do not need to use the word force at all. The law is complete without it, and is sufficient to enable us to calculate all the planetary motions. However, the



fact that the resultant acceleration is composed of a number of non-interfering parts, each depending on one other particle, and in the line joining  $A$  to that particle, strongly suggests to the mind the idea of an elastic pull. The mind likes to think of the elastic or of something; for, it is very difficult for the human mind to think at all unless it has something to think about. If Newton had found that the acceleration contributed by  $B$ , for example, was not in the line adjoining it to  $A$ ; if the acceleration had been at an angle of 45 degrees to this line, it would still have been possible to speak of the force due to  $B$  and  $A$ ; but, the mind would have lost much of



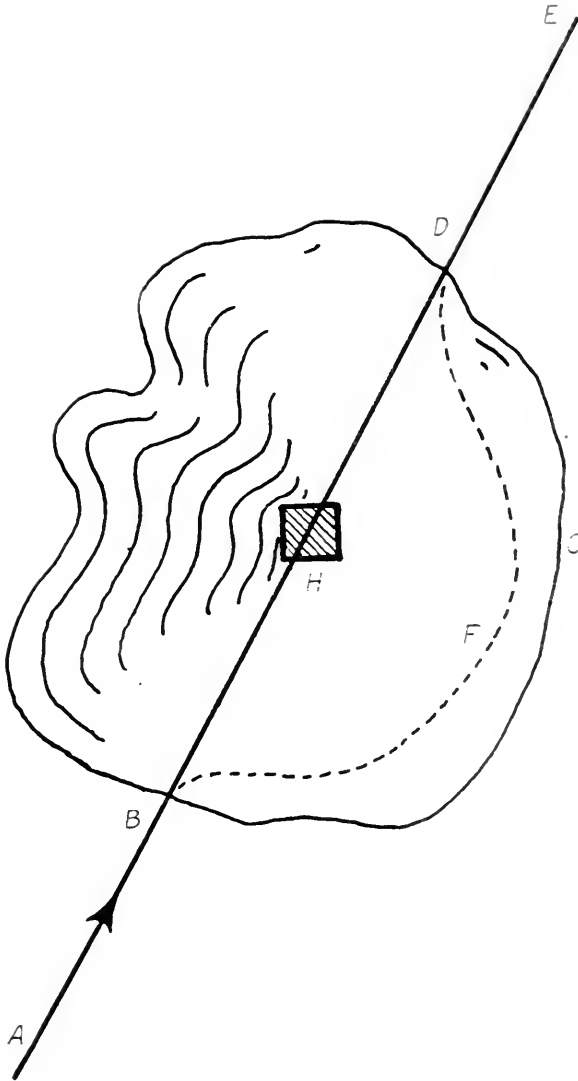
the inspiration which is derived from thinking of the elastic. A little further complication of the situation would result in our receiving still less benefit from the analogy of the elastic. We might hold on for some time, and force ourselves to think of a sort of modified elastic which could act in this way; but in order to do so, we should have to introduce notions more and more bizarre. It is by attempting to force all the laws of physics into the forms with which we were accustomed to deal in the first branch of that subject which we encountered in our youth that we are driven to speak of such curious concepts as masses varying with the velocity, and forces varying with velocity. These physical monstrosities are the symbols of a sort of protest on the part of nature's laws at being strained into clothes which were never made to fit them. The more the motion of the particle departs from the simple type of motion to be expected from the elastic, the less the mind gains from picturing the motion in terms of forces, until eventually, nothing but confusion results from an attempt to preserve the analogy.

From our youth up, we have been trained to view things from the standpoint that a body moves in a straight line with a constant velocity if no forces act upon it, and doubtless many of us have a very definite idea that we know what we mean by the statement. Our confidence in this surety might be a little shaken if we should imagine ourselves transported to some place where nothing is to be seen except the body whose motion we are discussing. How are we now to know whether a force is or is not acting on the body? It will surely not suffice to say that no force can be acting on it because we can see no apparatus around us to cause the force; for waves, or what not, may be travelling through this space and causing all sorts of phenomena. The more we think of the matter the more we realize that there is no meaning to the statement of whether a force is or is not acting upon the body unless we make one. In fact, the condition that the body is moving in a straight line with a constant velocity is an embodiment of what we *mean* by absence of force. This is the criterion of nothingness which the mind takes as its origin from which to elaborate its thoughts. The body moves in a straight line with constant velocity, and the mind is content with the spectacle: It is not tempted to do any thinking. If the body does not move in this way, the mind decides that a duty devolves upon it to do some thinking about the matter.



It thinks of the situation as a departure of the motion from one of the uniform rectilinear type, and such circumstances as it finds associated with this type of motion and not associated with the uniform linear motion it regards as causes of the departure. A full appreciation of the degree of arbitrariness of the mind in un-

FIG. 8.



consciously importing fundamental reality into the forces with which it deals is necessary if we are to understand the language of such a law of gravitation as that formulated by Einstein. It so often happens in arguments having to do with the fundamentals of physics, that the secret of understanding a certain viewpoint which at first repels us, because we think it lacks some reality which



we believe we find in some other viewpoint, is a more clear realization of the fact that the reality which we thought we saw was itself but a figment of the imagination.

I cannot of course enter, at this time, into the details of Einstein's theory of gravitation; but, I can possibly indicate, by a simple example, the point of view which it adopts in describing the law, and the relation of this point of view to the Newtonian.

Suppose that Fig. 8 represents a crater with a house  $H$  in the middle, and that a traveller sets out to go from  $A$  to  $E$  by the shortest path. He will not necessarily pursue the path  $ABHDE$  leading down to the bottom of the crater and through the house, because that may be too long. Neither will he necessarily walk right around the outside of the crater by the path  $ABCDE$  because that may also be too long. By taking some such course as  $ABFDE$ , crossing the crater part of the way down, it is possible that he will find a path which is shorter than any other, and this is the path he will take. Suppose now that, while this is true, we know nothing about it, and that we find ourselves seated high up in an airplane watching the spectacle. Of course, I shall not see the crater, as such. Everything will appear flat. I shall see the traveller going from  $A$  to  $E$  and shall wonder why he does not go straight across, and through the house. If I have been taught in my youth that a body moves in a straight line unless a force acts upon it, I shall conclude that the house repels him. Having come to this interesting conclusion, I shall ponder over the reason why the house repels him. Possibly I shall receive a sudden inspiration which will lead me to believe that the house contains a man who is provided with a hose, which he plays on the traveller compelling him to keep away from his property. I may be able to describe the traveller's path very accurately in terms of this hose. Now, if you are philosophically inclined, you may doubt the reality of this explanation, and ask me whether I am certain that there is really a hose in that house. Of course, if you press me hard enough, I shall find difficulty in proving that there is. If you worry me enough, however, I shall get very angry with you, and call you an impracticable philosopher; but, feeling the need of saying something to your arguments, I may finally talk to you in this way: "I care not whether there is or is not a hose in that house. So long as by picturing one there, and expressing the traveller's motion in terms of its influence I can predict results which are true, I am on



perfectly firm ground. I am responsible to no man for how I think, so long as my conclusions are correct." Having said this, I shall feel that I have justified my attitude and confounded you completely. I shall begin to feel a bit of a philosopher myself; but, I shall continue to enjoy, secretly, the picture of this hose and the various details of its actions. I shall think all sorts of things about it which I shall never dare tell you lest you should laugh at me. I shall wonder what the density of the liquid composing the hose-stream may be, what its boiling point may be and so forth. Now suppose that while I am doing all this, you should bring me some observations which show that the motion of the observer was not exactly what we thought it was. The difference might be very slight, but it might be of such a nature as to upset completely the simplicity of the action which I had imagined as going on by virtue of the hose. Of course, I shall first cling to my hose, but shall modify it slightly. I shall say, "Naturally this is no ordinary kind of hose. Possibly it does not push entirely in the direction in which the liquid travels." But, I shall have to face the situation that, while the discrepancies may be small in amount, they may be large in principle, and involve such radical alterations in my notions of the mechanism of the process that the hose which I shall have to picture will be radically different from any hose which I had ever seen. I shall go on in this way, modifying and adjusting the hose, making it more and more difficult to understand; and, forgetting that the original justification for its introduction was its apparent power to explain what was observed in terms of something which I thought I knew all about, I shall soon be in the position of expending 99 per cent. of my ingenuity in trying to understand the hose, leaving only 1 per cent. for the law of the traveller. Now suppose that, while I am doing this, and am feeling rather disheartened with my success, you should come to me and say, "I have made a discovery. I do not know why the man moves as he does, neither, I think, do you, but I have found out exactly how he does move. He is moving from *A* to *E* by a path which is the shortest distance between those two points, not as the crow flies, but across a crater whose form I can describe to you." Suppose you should say this, and should then add: "Now I am going to take this statement of the law as my starting point. If there is going to be any hose in the matter, it is the hose which is going to be explained in terms of this fundamental law, and not



the fundamental law which is going to be explained in terms of the hose." I think that I should have to admit that your attitude was, at least, reasonable.

Now it is an attitude something like this which is involved in the statement of Einstein's law of gravitation. It is true that here the statement is not made entirely in empirical terms. Its structure is adorned with many beauties into which I must not enter. But as regards the law itself, the language of its statement is not unlike that for the law of our traveller. It says that a planet, in going from one point to another, moves along a path which is the longest path between those points; but, alas, for the comfort of the non-mathematical mind, that path is not one in three dimensions, but it is a path in a certain non-euclidian four dimensional space of a certain type, whose fourth dimension is time, and whose properties are expressed in such a way as to conform to certain philosophical requirements of the theory of relativity.

The philosophers of by-gone ages said that the planets moved in circles because the circle is the perfection of symmetry, and we are inclined to laugh at their attitude; but, we see that the Einstein statement of the law of gravitation, avoiding as it does the mention of forces, and stating the law only in terms of the property of the path which the planet describes, has an element of the same attitude in it. Indeed, the law of the ancient philosophers would not have been so bad if it had been a little more explicit as to the sizes of the circles, and if they had omitted the "because."

---

**Measurement of Mercury Vapor Pressure by Means of the Knudsen Pressure Gauge.** C. F. HILL. (*Phys. Rev.*, Sept., 1922.)—Very discordant results have been obtained by different experimenters for the vapor pressure of mercury from 0° to 35° C. For the temperature zero the following values of the pressure in mm. of mercury have been published: .02, .015, .00019, .00047, .0004, .000184.

"The principle upon which the Knudsen gauge depends is that the molecules of a residual gas in a partial vacuum are thrown off from a heated platinum foil, and striking a light and suitably suspended vane exert a couple, thus producing a couple which may be read by means of an optical system." The Knudsen gauge was calibrated by means of a McLeod gauge. The mercury used was distilled several times. An accuracy of 3 per cent. in the results is claimed. The pressures for 0, 10, 20, 30 and 40 degrees are .000350, .000775, .00182, .00407 and .008, respectively. G. F. S.



# ON THE COMPRESSIBILITY OF MINERALS AND ROCKS AT HIGH PRESSURES.\*

BY

LEASON H. ADAMS and ERSKINE D. WILLIAMSON.

Geophysical Laboratory, Carnegie Institution of Washington.

THE elasticity of the earth's crust is an important branch of geophysics and is a subject of interest alike to physicists and to geologists. Very little information has been available concerning the elastic properties of rocks and their constituent minerals at high pressures such as exist at considerable depths below the surface of the earth. This information is of use in connection with problems of geophysics, among which may be mentioned the tidal deformation of the earth, the elastic yielding of the crust due to loads such as mountain masses or ice-sheets, the propagation of earthquake waves, and the effect of pressure on the stability of minerals. The deformation caused by a stress acting on a sufficiently homogeneous material may be referred to two constants, in the choice of which there is considerable latitude. Thus any two of the following properties: Compressibility, Young's modulus, rigidity, or Poisson's ratio, may be chosen to represent the elastic behavior of the material. The compressibility, that is the change of volume due to pressure, is the simplest to measure, at least at high pressures, and offers the easiest avenue of approach to the study of the elasticity of the earth's crust.

In this paper are presented the results of measurements of the decrease in volume of a number of rocks and minerals at pressures up to 12,000 megabars, corresponding to a depth of about 40 kilometres below the surface of the earth. From this decrease in volume the compressibility is calculated directly, and from the compressibility there is computed, for the rocks, an approximate value of the rigidity.

## METHOD.

The compressibilities were determined according to the method previously described,<sup>1</sup> and used for the measurement of the compressibilities of a number of solids including quartz, silica

---

\* Communicated by Dr. Arthur L. Day, Director of Laboratory and Associate Editor of this JOURNAL.

<sup>1</sup> Adams, Williamson, and Johnston, "The Determination of the Compressibility of Solids at High Pressures," *J. Am. Chem. Soc.*, 1918, **41**, 12-42.



glass, halite, and calcite. Briefly, the procedure is as follows: The solid is subjected to hydrostatic pressure in a thick-walled steel cylinder, or "bomb," and is entirely surrounded by kerosene (Fig.

FIG. 1.

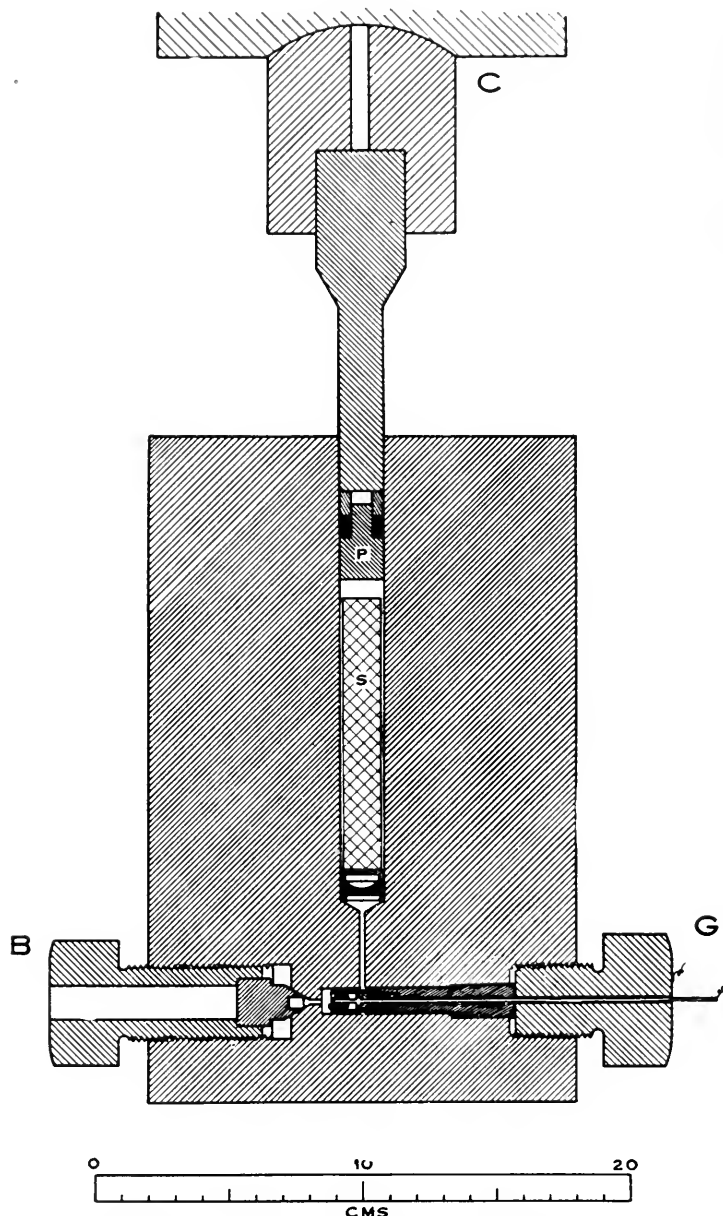


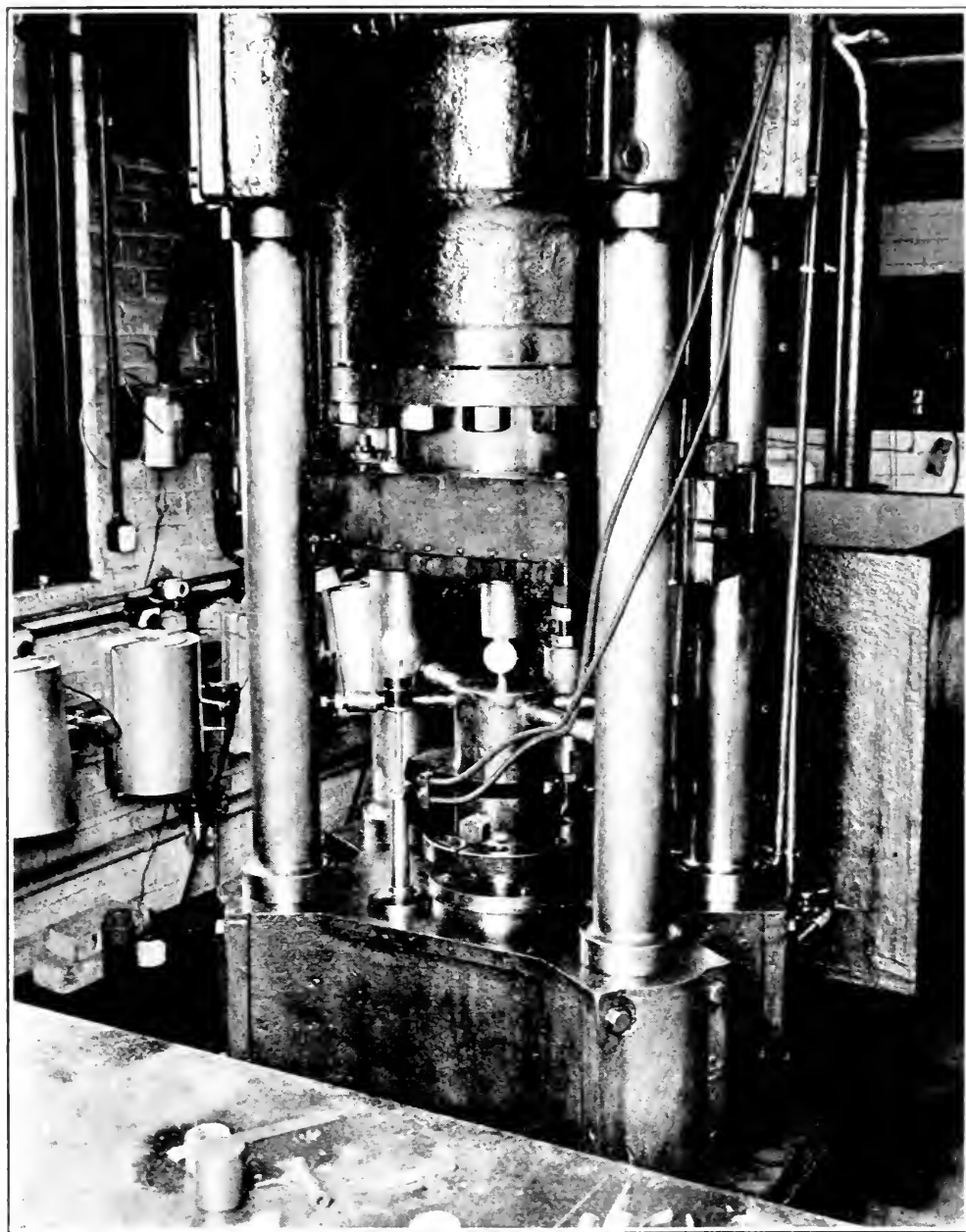
Diagram of vanadium steel bomb. The specimen, *S*, is completely surrounded by kerosene, and is subjected to pressure produced when the piston, *P*, is forced down by the motion of the press-platen, *C*. Pressure is measured by the resistance-gauge, *G*, and the volume-change of the kerosene plus specimen is determined by measuring the movement of the piston.

1) which transmits the pressure and insures that it shall be uniform in all directions, *i.e.*, purely hydrostatic. A piston provided with a leak-proof packing is forced into the bomb by means of a



hydraulic press. Its motion produces the pressure and also is a measure of the change of volume of the interior of the bomb. This volume-change is composed of three parts: (1) The decrease

FIG. 2.



Photograph of hydraulic press with bomb and appurtenances in position.

in volume of the sample itself, (2) the decrease in volume of the kerosene, and (3) the volume-change due to the distortion of the bomb and packing. The last two effects are compensated for by



an auxiliary experiment with a solid of known compressibility; the residue is the change in volume of the specimen. In effect, what is measured is the difference in compressibility of the material under investigation and that of the reference solid—soft steel—

FIG. 3.

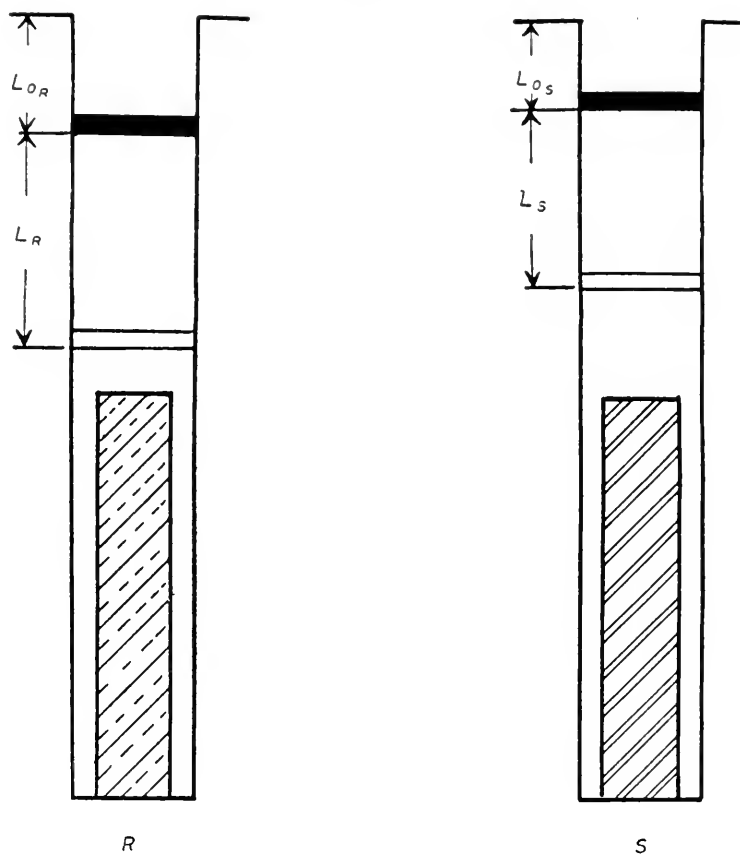


Diagram illustrating the initial and final positions of the piston in the two companion experiments: With the rock or mineral (R), and with the comparison steel (S).

the compressibility of which has been determined by a direct method,<sup>2</sup> and found to be  $0.60 \times 10^{-6}$  per megabar.<sup>3</sup>

<sup>2</sup> Vide P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 1911, **47**, 366; and E. Grüneisen, *Ann. Phys.*, [4] 1910, **33**, 1262.

A recent very accurate measurement by Bridgman (*Proc. Am. Acad. Arts. Sci.*, 1923, **58**, 174) gives  $0.577 \times 10^{-6}$  per megabar for the compressibility of iron containing only 0.03 per cent. impurity. If this value be accepted, the values given in this paper should be lowered by  $0.02 \times 10^{-6}$ , but it is not impossible that the compressibility of soft steel is a trifle higher than that of pure iron.

<sup>3</sup> For high pressures there are three units in common use: The megabar, the atmosphere, and the kilogram per square centimetre. For several reasons, among which is the circumstance that the megabar is independent of the force of gravity, we have used that unit. One megabar =  $1.0197 \text{ kg./cm.}^2 = 0.9869 \text{ atm.}$  at Washington, D. C.



The volume-change, that is, the movement of the piston, is measured to within a few thousandths of a millimetre by a dial-gage attached to the piston; the pressure is measured to 1 megabar by an electrical resistance pressure-gage. The compressibility,  $\beta$ , is here defined as  $-\frac{1}{V_0} \frac{dV}{dP}$  where  $-dV$  is the diminution in volume for a given increment of pressure  $dP$ , and  $V_0$  is the volume at some standard pressure and temperature. The unit of pressure being the megabar, compressibility is expressed as the relative volume-change per megabar. Thus, a compressibility of  $1 \times 10^{-6}$  means that the volume of the substance in question is reduced by one-millionth of its value (at the standard pressure) for each megabar increase of pressure.

Whenever possible, the materials to be investigated were fashioned into cylinders 10 cm. long and 1.6 cm. in diameter. In other cases the material in the form of coarse fragments was held in a capsule made of thin sheet copper closed at the bottom and open at the top. A diamond core-drill proved a great convenience in making cylinders of the rocks and some of the minerals. In all cases the cylinders were brought to their final size by grinding.

From the readings of pressure and piston-displacement the decrease in volume was calculated by the formula:

$$-\frac{\Delta V_r}{V_r} = -\frac{\Delta V_s}{V_s} \frac{V_s}{V_r} + \frac{A}{V_r} \left\{ \Delta L(1 + \alpha P) + \alpha \Delta L_0(P - P_0) - \frac{\Delta V_k}{V_k} [\Delta L_0(1 + \alpha P) + Q] \right\} \quad (1)$$

which gives the fractional decrease in volume,  $-\Delta V_r/V_r$  of the material at the pressure  $P$  as compared with  $V_r$  the volume at the arbitrary initial pressure  $P_0$  (2000 megabars). In this equation  $-\Delta V_s/V_s$  is the fractional decrease in volume of the reference substance (steel) as determined from  $\beta_s = -\frac{\Delta V_s}{V_s} \frac{1}{P - P_0} = 0.60 \times 10^{-6}$  per megabar. The cross-section of the hole in the bomb is  $A$  at  $P = 0$ ;  $\alpha = \frac{1}{A_0} \frac{dA}{dP} = 1.2 \times 10^{-6}$  per megabar;  $\Delta L$  is written for  $L_r - L_s$  and is the difference of levels at the pressure  $P$  (Fig. 2);  $\Delta L_0$  is the difference of levels at the initial pressure  $P_0$ ;  $-\frac{\Delta V_k}{V_k}$  is the fractional decrease of volume of the kerosene between the pressures  $P_0$  and  $P$ ; and  $Q = \frac{V_r - V_s}{A}$ .  $V_r$ ,  $V_s$  and  $V_k$  are respectively the volumes of the rock, the steel, and the kerosene at the initial pressure  $P_0$ .



It should be borne in mind that here  $\Delta V_r/V_r$  and also  $\beta$  refer to the fractional volume-change in terms of the volume at  $P_0$ , that is, at 2000 megabars. If it is desired to refer the fractional volume-change and  $\beta$  to the volume at  $P = 0$ , the values here given for  $\Delta V_r/V_r$  and for  $\beta$  must be multiplied by  $V_r/V_0$ , that is, by  $V_{2000}/V_0$ , the ratio of the volumes at the two pressures. It may be noted, however, that for most solids the difference between these two values of  $\beta$  is unimportant.

Equation (1) is in convenient form for calculating the volume-changes of the cylindrical samples, but a slight modification of (1) is more convenient in the case of the materials in granular form. Writing

$$V_r = V_{Cu} + V'_r$$

$V_{Cu}$  being the volume of the capsule at  $P_0$ , and  $V'_r$  that of the sample at the same pressure, equation (1) becomes:

$$-\frac{\Delta V'_r}{V'_r} = \frac{-(-\Delta V_{Cu}) - \Delta V_s + A \left\{ \Delta L(1 + \alpha P) + \alpha \Delta L_0(P - P_0) - \frac{\Delta V_k}{V_k} [\Delta L_0(1 + \alpha P) + Q] \right\}}{V'_r} \quad (2)$$

which is in the form actually used for calculating the changes in volume of the granular materials.

#### DESCRIPTION OF MATERIALS USED.

We have studied the following minerals and rocks, of which some of the characteristic properties are given. The densities—as well as the volumes, which are necessary for the calculation of the compressibilities—were determined from the loss in weight (corrected to vacuum) when immersed in water, and are expressed as true densities. For the porous materials an approximate value of the porosity was obtained by noting the increase in weight of the material when saturated with kerosene at a pressure of several thousand megabars. The letter C after the name indicates that a cylinder was made of the material; G, that the substance was used in granular form.

*Microcline*. (C)—A large creamy white crystal from Topsham, Maine, kindly furnished by Professor G. P. Merrill of the U. S. National Museum. Density at 25°, 2.557. Contains 8 to 10 per cent. albite<sup>4</sup>; perthitic intergrowth parallel to {100}.

<sup>4</sup> Kindly determined by Dr. N. L. Bowen.



*Oligoclase.* (C)—A large white crystal from Lindstöl, Söndeled, Norway; collected by Dr. Olaf Andersen. Density at  $25^{\circ}$ , 2.638. Refractive indices and extinction angles in oriented sections correspond<sup>4</sup> to  $\text{Ab}_{78}\text{An}_{22}$ .

*Labradorite.* (C)—A fine specimen of the well-known material from Nain, Labrador. Obtained from Ward's Natural Science Establishment. Density at  $26^{\circ}$ , 2.695. Refractive indices and extinction angles in oriented sections correspond<sup>4</sup> to  $\text{Ab}_{48}\text{An}_{52}$ . Contains a small amount of inclusions of augite and ilmenite, which accounts for the fact that the density is about 0.015 gram/cm.<sup>3</sup> higher than would be expected from the composition of the mineral.

*Phlogopite Mica.* (C)—Large crystal with the usual rough prismatic faces; obtained through Dr. N. L. Bowen, from Frontenac County, Ontario, Canada. A cylinder was cut with its axis parallel to the cleavage, and was held together with fine wire. Density at  $25^{\circ}$ , 2.877.

*Enstatite.* (CG)—Light smoky gray crystal from Espedalen, Vegaardsheien, west of Risör, Norway; collected by Dr. Olaf Andersen. Density at  $25^{\circ}$ , 3.254. Composition:<sup>5</sup>  $\text{SiO}_2$ , 57.28;  $\text{Al}_2\text{O}_3$ , 0.90;  $\text{Fe}_2\text{O}_3$ , 0.42;  $\text{FeO}$ , 6.43;  $\text{MgO}$ , 34.94;  $\text{CaO}$ , 0.13;  $\text{Na}_2\text{O}$ , 0.22;  $\text{K}_2\text{O}$ , 0.01;  $\text{H}_2\text{O}+$ , 0.13;  $\text{TiO}_2$ , 0.05. Minor constituents being neglected, this corresponds to:  $\text{MgSiO}_3$ , 88;  $\text{FeSiO}_3$ , 12.

*Hypersthene.* (G)—A large crystal from Nain, Labrador; kindly furnished by Mr. E. V. Shannon of the U. S. National Museum. Density at  $29^{\circ}$ , 3.415. Composition:<sup>5</sup>  $\text{SiO}_2$ , 51.81;  $\text{Al}_2\text{O}_3$ , 2.16;  $\text{Fe}_2\text{O}_3$ , 4.52;  $\text{FeO}$ , 13.96;  $\text{MgO}$ , 24.57;  $\text{CaO}$ , 1.95;  $\text{Na}_2\text{O}$ , 0.39;  $\text{K}_2\text{O}$ , 0.03;  $\text{H}_2\text{O}+$ , 0.19;  $\text{TiO}_2$ , 0.76;  $\text{MnO}$ , 0.16. Except for minor constituents, this corresponds to:  $\text{MgSiO}_3$ , 70;  $\text{FeSiO}_3$ , 30.

*Diopside.* (G)—Nearly colorless, transparent crystals from Ham Island, Alaska. Density at  $28^{\circ}$ , 3.257. This is the material investigated by Allen and White.<sup>6</sup> Composition:  $\text{SiO}_2$ , 54.65;

<sup>5</sup> H. S. Washington and H. E. Merwin, *Am. Mineral.*, 8, 1923. We wish to express our indebtedness to Doctor Washington for his kindness in making the analysis of this material and of several other rocks and minerals which we have used.

<sup>6</sup> E. T. Allen and W. P. White, *Am. J. Sci.*, 1909, 27, 13.



$\text{Fe}_2\text{O}_3$ , 0.13;  $\text{CaO}$ , 25.27;  $\text{MgO}$ , 18.78;  $\text{Na}_2\text{O}$ , 0.03;  $\text{K}_2\text{O}$ , 0.07;  $\text{H}_2\text{O}$ , 1.45.

*Augite.* (G)—Rough black crystals of the habit usual to loose, ejected volcanic augites. Obtained through Dr. H. S. Washington from Professor F. Millosevich of Rome, who collected the material at Fosso Tivolato, Alban Hills, Italy. Density at  $28^\circ$ , 3.373. Composition:<sup>7</sup>  $\text{SiO}_2$ , 48.11;  $\text{Al}_2\text{O}_3$ , 5.45;  $\text{Fe}_2\text{O}_3$ , 4.42;  $\text{FeO}$ , 3.74;  $\text{MgO}$ , 12.03;  $\text{CaO}$ , 24.50;  $\text{Na}_2\text{O}$ , 0.46;  $\text{K}_2\text{O}$ , none;  $\text{H}_2\text{O}^+$ , 0.09;  $\text{TiO}_2$ , 1.19;  $\text{Cr}_2\text{O}_3$ , 0.06;  $\text{MnO}$ , 0.09.

*Actinolite.* (G)—A large crystal from Kragerö, Norway; collected by Dr. Olaf Andersen. Density at  $28^\circ$ , 3.079. Composition:<sup>5</sup>  $\text{SiO}_2$ , 51.86;  $\text{Al}_2\text{O}_3$ , 3.81;  $\text{Fe}_2\text{O}_3$ , 2.19;  $\text{FeO}$ , 5.97;  $\text{MgO}$ , 19.40;  $\text{CaO}$ , 10.73;  $\text{Na}_2\text{O}$ , 2.16;  $\text{K}_2\text{O}$ , 0.28;  $\text{H}_2\text{O}^+$ , 0.98;  $\text{TiO}_2$ , 1.92;  $\text{MnO}$ , 0.04; (F, 0.46).

*Pyrite.* (C)—Large cubic crystal from Leadville, Colorado. Density at  $25^\circ$ , 4.992.

*Diamond.* (G)—Nearly colorless, rough stones<sup>8</sup> weighing about 1/6 carat or 0.05 g. each. Density at  $25^\circ$ , 3.516.

*Westerly Granite.* (C)—Fine-grained pink granite from Westerly, Rhode Island. Cylinder used by us was cut down from one used by Adams and Coker.<sup>9</sup> Density at  $19^\circ$ , 2.616. Porosity, 0.7 per cent. Approximate composition:<sup>10</sup>  $\text{SiO}_2$ , 72.26;  $\text{Al}_2\text{O}_3$ , 13.58;  $\text{Fe}_2\text{O}_3$ , 2.97;  $\text{FeO}$ , 0.75;  $\text{MgO}$ , 0.03;  $\text{CaO}$ , 1.24;  $\text{Na}_2\text{O}$ , 2.18;  $\text{K}_2\text{O}$ , 5.69;  $\text{H}_2\text{O}^+$ , 0.57;  $\text{H}_2\text{O}^-$ , 0.09.

Norm: Quartz, 35.0; orthoclase, 33.9; albite, 18.3; anorthite, 6.1; corundum, 1.5; hypersthene, 0.1; magnetite, 2.3; hematite, 1.4.

<sup>7</sup> H. S. Washington and H. E. Merwin, *Am. Mineral*, 8, 1923.

<sup>8</sup> We are greatly indebted to Mr. Hans Brassler, of New York City, for lending us nearly 60 grams of rough diamonds, and we desire to record our sincere appreciation of his courtesy.

<sup>9</sup> "An Investigation into the Elastic Constants of Rocks, More Especially with Reference to Cubic Compressibility," Frank D. Adams and Ernest G. Coker, Carnegie Institution of Washington, Publ. No. 46.

We were very fortunate in being able to work with the identical samples used by Adams and Coker, not only the Sudbury diabase but also the Westerly granite and the New Glasgow gabbro. We are very grateful to Professor Adams for his kindness in furnishing us these materials.

<sup>10</sup> Analysis by I. A. Williams of rock from same locality. Quoted in Professional Paper No. 99, "Chemical Analyses of Igneous Rocks," by Henry S. Washington. Analysis No. 1, p. 165.



Mode: Quartz, 26; alkaline feldspars, mostly microcline, 70; mica, largely biotite, 4.

*Stone Mountain Granite.* (C)—Fine-grained gray granite from Stone Mountain near Atlanta, Georgia. Specimen taken from the block obtained by Day, Sosman, and Hostetter,<sup>11</sup> for the measurement of densities at high temperatures. Density at 25°, 2.633. Porosity, 0.6 per cent. The approximate composition<sup>12</sup> is as follows: SiO<sub>2</sub>, 71.66; Al<sub>2</sub>O<sub>3</sub>, 16.05; Fe<sub>2</sub>O<sub>3</sub>, 0.86; FeO, not determined; MgO, 0.17; CaO, 1.07; Na<sub>2</sub>O, 4.66; K<sub>2</sub>O, 4.92; H<sub>2</sub>O+, 1.00.

Norm: Quartz, 22.8; orthoclase, 28.9; albite, 39.3; anorthite, 5.3; corundum, 1.1; hypersthene, 1.7.

Mode: Quartz, 20; microcline, 40; plagioclase, Ab<sub>85</sub>An<sub>15</sub>, 30; mica, nearly all muscovite, 10.

*Washington Granite.* (C)—Coarse-grained gray biotite granite, somewhat gneissoid, collected by us at quarry on Tilden Street, near Connecticut Avenue, Washington, D. C. Density at 25°, 2.739. Porosity, 0.6 per cent. Composition:<sup>13</sup> SiO<sub>2</sub>, 67.46; Al<sub>2</sub>O<sub>3</sub>, 14.22, Fe<sub>2</sub>O<sub>3</sub>, 1.33; FeO, 3.24; MgO, 2.85; CaO, 3.72; Na<sub>2</sub>O, 2.88; K<sub>2</sub>O, 2.84; H<sub>2</sub>O+, 0.57; H<sub>2</sub>O-, 0.12; TiO<sub>2</sub>, 0.47; P<sub>2</sub>O<sub>5</sub>, 0.31; MnO, 0.08.

Norm: Quartz, 26.5; orthoclase, 16.7; albite, 24.6; anorthite, 16.4; corundum, 0.3; hypersthene, 11.3; magnetite, 1.9; ilmenite, 0.9; apatite, 0.7.

Mode (Rather difficult to determine definitely from one thin section, on account of coarseness of grain): Quartz, 32; orthoclase, 18; plagioclase, Ab<sub>80</sub>An<sub>20</sub>, 35; mica, nearly all biotite, 9; epidote, 6.

*Obsidian.* (C)—The well-known black material from Obsidian Cliff, Yellowstone National Park, obtained through Dr. F. E. Wright. Density at 25°, 2.333. Approximate composi-

<sup>11</sup> Arthur L. Day, R. B. Sosman, and J. C. Hostetter, *Am. J. Sci.*, 1914, 37, 1-39; *Neues Jahrb. Beil. Bd.*, 1915, 40, 119-162.

<sup>12</sup> Analysis of rock from same locality by R. L. Packard. *Vide* Washington, "Chemical Analyses of Igneous Rocks," U. S. Geol. Surv., Professional Paper No. 99. Analysis No. 51, p. 173.

<sup>13</sup> H. S. Washington, "The Granites of Washington, D. C.," *J. Wash. Acad. Sci.*, 1921, 11, 459-470.



tion:<sup>14</sup> SiO<sub>2</sub>, 74.70; Al<sub>2</sub>O<sub>3</sub>, 13.72; Fe<sub>2</sub>O<sub>3</sub>, 1.01; FeO, 0.62; MgO, 0.14; CaO, 0.78; Na<sub>2</sub>O, 3.90; K<sub>2</sub>O, 4.02; H<sub>2</sub>O+, 0.62; FeS<sub>2</sub>, 0.40.

Norm: Quartz, 34.9; orthoclase, 23.4; albite, 33.0; anorthite, 3.9; corundum, 1.5; hypersthene, 0.7; magnetite, 1.4.

Mode: All glass.

*Gabbro.* (C)—This specimen, from New Glasgow, Quebec, is identical with the material used by Adams and Coker and described in the publication cited. It is a dark greenish color, coarse-grained, and somewhat variably mottled. Density at 23°, 3.106. Composition:<sup>15</sup> SiO<sub>2</sub>, 44.67; Al<sub>2</sub>O<sub>3</sub>, 20.74; Fe<sub>2</sub>O<sub>3</sub>, 2.13; FeO, 4.10; MgO, 16.97; CaO, 9.90; Na<sub>2</sub>O, 1.15; K<sub>2</sub>O, 0.59; H<sub>2</sub>O+, 0.15; H<sub>2</sub>O-, 0.06; TiO<sub>2</sub>, 0.09; P<sub>2</sub>O<sub>5</sub>, none; MnO, n.d.

Norm: Orthoclase, 3.3; albite, 10.0; anorthite, 49.2; hypersthene, 1.4; olivine, 33.1; magnetite, 3.0; ilmenite, 0.2.

Mode: There appears to be 25 per cent. plagioclase, Ab<sub>35</sub>An<sub>65</sub>; 40 per cent. hypersthene, and 35 per cent. olivine (Adams and Coker<sup>16</sup> report: Not over one-quarter plagioclase, the remaining minerals being augite and rhombic pyroxene in equal amounts.) Neither of these estimates agrees with the norm, which is probably due to lack of uniformity of the rock.

*Sudbury Diabase.* (C)—This was part of one of the cylinders used by F. D. Adams and E. G. Coker in their investigation of the elastic constants of certain rocks.<sup>17</sup> This rock is a moderately coarse-grained diabase. It comes from the Murray mine near Sudbury, Ontario, and is fully described by Adams and Coker. Density at 28°, 3.002. Porosity, 0.05 per cent. Composition:<sup>18</sup> SiO<sub>2</sub>, 48.40; Al<sub>2</sub>O<sub>3</sub>, 16.07; Fe<sub>2</sub>O<sub>3</sub>, 2.10; FeO, 11.91; MgO, 5.68; CaO, 7.87; Na<sub>2</sub>O, 4.61; K<sub>2</sub>O, 0.48; H<sub>2</sub>O+, 0.38; H<sub>2</sub>O-, 0.09; TiO<sub>2</sub>, 2.53; P<sub>2</sub>O<sub>5</sub>, 0.16; MnO, 0.11.

Norm: Orthoclase, 2.8; albite, 27.5; anorthite, 22.0; nephelite, 6.1; diopside, 13.6; olivine, 17.4; magnetite, 3.0; ilmenite, 4.9; apatite, 0.3.

Mode: Plagioclase, Ab<sub>35</sub>An<sub>65</sub>, 70; olivine, 15; augite, 10; magnetite, 5.

<sup>14</sup> Analysis by J. E. Whitfield of an obsidian from same locality. *Vide* H. S. Washington, "Chemical Analyses of Igneous Rocks," U. S. Geol. Surv., Professional Paper No. 99. Analysis No. 18, p. 63.

<sup>15</sup> H. S. Washington, unpublished.

<sup>16</sup> Adams and Coker, *op. cit.*, p. 55.

<sup>17</sup> *Op. cit.*

<sup>18</sup> H. S. Washington, unpublished.



*Palisade Diabase.* (C)—Fine-grained diabase from quarry one mile north of Granton, New Jersey. This is a specimen of the rock used by Day, Sosman, and Hostetter in their investigation of mineral and rock densities at high temperatures.<sup>19</sup> Density at 25°, 2.975. Porosity, 0.06 per cent. This rock has been described by Lewis<sup>20</sup> and probably corresponds closely to his analyses XII and XIII, p. 121 of his report. Analysis XIII is as follows:<sup>21</sup> SiO<sub>2</sub>, 50.34; Al<sub>2</sub>O<sub>3</sub>, 15.23; Fe<sub>2</sub>O<sub>3</sub>, 2.82; FeO, 11.17; MgO, 5.81; CaO, 9.61; Na<sub>2</sub>O, 2.93; K<sub>2</sub>O, 1.02; H<sub>2</sub>O+, 0.07; H<sub>2</sub>O-, 0.19; TiO<sub>2</sub>, 1.56; P<sub>2</sub>O<sub>5</sub>, 0.20; MnO, 0.14.

Norm: Orthoclase, 6.1; albite, 24.6; anorthite, 25.3; diopside, 18.0; hypersthene, 13.6; olivine, 5.8; magnetite, 4.2; ilmenite, 3.0; apatite, 0.3.

Mode: Plagioclase, Ab<sub>40</sub>An<sub>60</sub>, 49; augite, 50; magnetite, 1.

*Basalt.* (C)—Dense, black, non-porphyrific basalt from Hatfield and Weldon's quarry, Scotch Plains, New Jersey. Density at 26°, 2.911. Porosity, 0.9 per cent. Its composition is probably represented by analysis V of Lewis' report.<sup>22</sup> This analysis is as follows: SiO<sub>2</sub>, 51.84; Al<sub>2</sub>O<sub>3</sub>, 15.11; Fe<sub>2</sub>O<sub>3</sub>, 1.78; FeO, 8.31; MgO, 7.27; CaO, 10.47; Na<sub>2</sub>O, 1.87; K<sub>2</sub>O, 0.34; H<sub>2</sub>O+, 1.33; H<sub>2</sub>O-, 0.56; TiO<sub>2</sub>, 1.22; P<sub>2</sub>O<sub>5</sub>, 0.13; MnO, 0.09.

Norm: Quartz, 5.0; orthoclase, 2.2; albite, 16.2; anorthite, 31.4; diopside, 16.3; hypersthene, 22.1; magnetite, 2.6; ilmenite, 2.3; apatite, 0.3.

Mode: Plagioclase, Ab<sub>45</sub>An<sub>55</sub>, 30; augite, 50; glass, 20.

*Marble.* (C)—Pure white, coarse-grained material from Ule Creek, Gunnison County, Colorado. Part of a large piece given to us by Professor G. P. Merrill. Porosity, 0.8 per cent. Density at 25°, 2.708.

*Serpentine.* (*Talc schist*) (C)—This material is commonly called "Alberene Stone," and comes from Alberene, Virginia. Density at 19°, 2.875.

It consists of about 50 per cent. talc, 15 per cent. calcite, 15 per cent. serpentine, and smaller amounts of chlorite and magnetite.

<sup>19</sup> Day, Sosman, and Hostetter, *op. cit.*

<sup>20</sup> Geol. Surv. New Jersey, Ann. Report, 1907, 97-168.

<sup>21</sup> Cf. H. S. Washington, "Chemical Analyses of Igneous Rocks," U. S. Geol. Surv., Professional Paper No. 99. Analysis No. 15, p. 607.

<sup>22</sup> *Op. cit.*, p. 159, Cf. H. S. Washington, "Chemical Analyses of Igneous Rocks," U. S. Geol. Surv., Professional Paper No. 99. Analysis No. 22, p. 641.



*Plate Glass.* (C)—A cylinder was ground from a piece of plate glass. Density at  $25^{\circ}$ , 2.530. This particular glass was not analyzed, but is known to have approximately the following composition:  $\text{SiO}_2$ , 73;  $\text{CaO}$ , 12;  $\text{Na}_2\text{O}$ , 15.

*Cast Iron.* (C)—This specimen was soft gray cast iron. Density at  $23^{\circ}$ , 7.193.

#### EXPERIMENTAL RESULTS.

*Minerals.*—The results of the measurements on the various minerals are presented in Tables I and II, and summarized in Table III. Table I contains the results obtained with the minerals which were used in the form of cylinders. In the columns of this table are successively: The pressure in megabars; the corresponding value of  $\Delta L$ , that is, of  $L_r - L_s$ , the difference in piston-displacements in the experiment with the comparison steel and in the experiment with the material under investigation;  $\Delta L$  (corrected), that is the value of the term enclosed within the brackets in equation (1);  $-(\Delta V_r/V_r - \Delta V_s/V_r)$ , the difference between the relative volume-changes of the steel and the given material; and  $-(\Delta V_r/V_r)$ , the relative decrease in volume of the mineral at the given pressure. The figures in the sixth and seventh columns will be explained later. For the measurements in this table the volume of the comparison steel cylinder was 20,054 cubic millimetres at  $P = 1$  megabar. Below each sub-heading are given: The value of  $\Delta L_0$  for that experiment;  $V$ , the volume of the mineral at  $P = 1$ ; and  $Q$ , (that is,  $(V_r - V_s)/A$ ), where  $V_r$  and  $V_s$  are the volumes at  $P = 2000$ . Table II, which is for the minerals used in the granular form, is similar to Table I except that the figures corresponding to column 4 of Table I do not appear. This is due to the fact that equation (2) is the one used for calculating the volume-changes of the minerals in granular form. The volume of the comparison steel was 10,674 mm.<sup>3</sup> at  $P = 1$ , except for the series with diamond, in which case the volume was 9879 mm.<sup>3</sup>  $\Delta L_0$  and  $Q$  have the same meaning as in Table I;  $V'$  is the volume of mineral itself;  $V_{Cu}$  is the volume of the copper capsule, and  $V$  is the sum of the two, all at  $P = 1$ .

The relative volume-change at the given pressure as obtained<sup>23</sup> from equation (1) or (2) is shown in column 5 of Table I and

<sup>23</sup> For further details, including the compressibility of the kerosene used, see Adams, Williamson, and Johnston, *op. cit.*



TABLE I.

*Experimental Results for Minerals in Cylindrical Form. Volume of Reference Steel, 20,054 mm.<sup>3</sup> at  $P=0$ .*

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r - \Delta V_s/V_r)$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
OLIGOCLASE.						
$\Delta L_0 = -0.12$ $V = 20,122$ $Q = 0.09$ $10^4 a = -.2$ $10^6 b = 1.725$ $10^{10} c = 0.057$						
12,000	0.931	0.938	0.01080	0.01630	0.01666	1.4
11,000	.830	.836	964	1504	1504	.0
10,000	.735	.739	851	1331	1341	-1.0
9,000	.658	.660	760	1180	1178	.2
8,000	.555	.556	641	1001	1011	-1.0
7,000	.475	.475	547	847	846	.1
6,000	.372	.372	428	666	679	-1.3
5,000	.282	.282	325	505	510	-.5
4,000	.196	.195	224	344	341	.3
3,000	.102	.101	116	176	170	.4
2,000	0.000	0.000	0.00000	0.00000	-0.00002	.2

## OLIGOCLASE.

$\Delta L_0 = 0.11$   $V = 20,122$   $Q = 0.09$   $10^4 a = .7$   $10^6 b = 1.726$   $10^{10} c = 0.080$

7,840	0.523	0.551	0.00635	0.00989	0.00994	-.5
6,860	.448	.473	545	839	834	.5
5,880	.356	.377	434	669	671	-.2
4,900	.276	.292	336	512	508	.4
3,920	.186	.197	227	345	342	.3
2,940	.100	.105	121	180	176	.4
1,960	0.000	0.000	0.00000	0.00000	0.00007	-.7

## OLIGOCLASE.

$\Delta L_0 = 0.70$   $V = 20,107$   $Q = 0.02$   $10^4 a = 0.0$   $10^6 b = 1.691$   $10^{10} c = 0.115$

12,000	0.700	0.826	0.00971	0.01571	0.01576	-.5
10,000	.578	.688	809	1289	1279	1.0
8,000	.427	.516	607	967	973	-.6
6,000	.287	.353	415	655	658	-.3
4,000	.144	.183	215	335	334	.1
3,000	.071	.091	107	167	168	-.1
2,000	0.000	0.000	0.00000	0.00000	0.00000	.0

## LABRADORITE.

$\Delta L_0 = -0.08$   $V = 20,216$   $Q = 0.54$   $10^4 a = .5$   $10^6 b = 1.531$   $10^{10} c = 0.104$

12,000	0.645	0.724	0.00837	0.01437	0.01432	.5
11,000	.576	.649	750	1290	1298	-.8
10,000	.518	.587	678	1158	1161	-.3
9,000	.474	.535	619	1039	1026	1.3
8,000	.398	.453	525	885	886	.1
7,000	.342	.389	451	751	745	.6
6,000	.262	.301	348	588	601	-1.3
5,000	.202	.234	271	451	455	-.4
4,000	.143	.167	193	313	307	.6
3,000	.079	.091	105	165	157	.8
2,000	0.000	0.000	0.00000	0.00000	0.00005	-.5



TABLE I.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r$ $-\Delta V_s/V_r)$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
-------------------------	------------	-----------------------	--	-------------------------------	--------------------------------	---------------------

## LABRADORITE.

$$\Delta L_0 = 0.015 \quad V = 20,216 \quad Q = 0.54 \quad 10^4 a = .4 \quad 10^6 b = 1.512 \quad 10^{10} c = 0.128$$

7,840	0.354	0.419	0.00485	0.00839	0.00849	-1.0
6,860	.309	.366	423	717	715	.2
5,880	.252	.301	348	583	578	.5
4,900	.187	.226	262	438	438	.0
3,920	.135	.164	189	307	296	1.1
2,940	.056	.071	082	141	151	-1.0
1,960	0.000	0.000	0.00000	0.00000	0.00004	-.4

## LABRADORITE.

$$\Delta L_0 = -0.06 \quad V = 20,216 \quad Q = 0.54 \quad 10^4 a = -0.2 \quad 10^6 b = 1.482 \quad 10^{10} c = 0.110$$

12,000	0.569	0.647	0.00756	0.01356	0.01371	-1.5
10,000	.494	.562	660	1140	1114	2.6
8,000	.359	.414	484	844	848	-.4
6,000	.228	.270	316	556	573	-1.7
4,000	.120	.145	170	290	290	.0
3,000	.061	.074	87	147	145	.2
2,000	0.000	0.000	0.00000	0.00000	-0.00002	.2

## MICROCLINE.

$$\Delta L_0 = 0.07 \quad V = 20,074 \quad Q = -0.16 \quad 10^4 a = .3 \quad 10^6 b = 1.880 \quad 10^{10} c = 0.128$$

12,000	0.998	1.000	0.01154	0.01754	0.01755	-.1
11,000	.915	.915	1056	1596	1591	.5
10,000	.817	.816	942	1422	1425	-.3
9,000	.728	.726	838	1258	1264	-.6
8,000	.631	.628	725	1085	1085	.0
7,000	.532	.527	609	909	911	-.2
6,000	.428	.423	488	728	734	-.6
5,000	.334	.330	382	562	555	.7
4,000	.225	.222	256	376	374	.2
3,000	.117	.115	133	193	190	.3
2,000	0.000	0.000	0.00000	0.00000	0.00003	-.3

## MICROCLINE.

$$\Delta L_0 = -0.20 \quad V = 20,074 \quad Q = 0.13 \quad 10^4 a = 1.0 \quad 10^6 b = 1.865 \quad 10^{10} c = 0.095$$

7,840	0.653	0.622	0.00718	0.01072	0.01075	-.3
6,860	.554	.526	607	901	902	-.1
5,880	.449	.423	489	724	727	-.3
4,900	.348	.327	378	554	551	.3
3,920	.243	.228	263	381	372	.9
2,940	.128	.119	137	196	192	.4
1,960	0.000	0.000	0.00000	0.00000	0.00010	-1.0



TABLE I.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r - \Delta V_s/V_s)$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
ENSTATITE.						
$\Delta L_0 = -0.47$ $V = 20,065$ $Q = -0.05$ $10^4a = 1.4$ $10^6b = 1.000$						
12,000	0.434	0.356	0.00411	0.01011	0.01014	— .3
11,000	.390	.316	367	907	914	— .7
10,000	.355	.285	329	809	814	— .5
9,000	.322	.257	297	717	714	.3
8,000	.281	.222	256	616	614	.2
7,000	.249	.197	223	523	514	.9
6,000	.202	.157	181	421	414	.7
5,000	.160	.124	143	323	314	.9
4,000	.109	.082	095	215	214	— .1
3,000	.060	.046	053	113	114	.1
2,000	0.000	0.000	0.00000	0.00000	0.00014	— 1.4
ENSTATITE.						
$\Delta L_0 = -0.60$ $V = 20,065$ $Q = -0.05$ $10^4a = -.6$ $10^6b = 1.080$						
7,840	0.311	0.238	0.00275	0.00629	0.00629	.0
6,860	.267	.201	232	526	523	.3
5,880	.214	.158	182	417	418	— .1
4,900	.158	.113	130	306	312	— .6
3,920	.118	.086	099	217	206	1.1
2,940	.043	.024	028	087	100	— 1.3
1,960	0.000	0.000	0.00000	0.00000	— 0.00006	.6
MICA.						
$\Delta L_0 = 0.54$ $V = 18,468$ $Q = -7.14$ $10^4a = 1.4$ $10^6b = 2.270$ $10^{10}c = 0.174$						
7,840	1.450	0.735	0.00923	0.01277	0.01289	— 1.2
6,860	1.264	.631	796	1090	1085	.5
5,880	1.059	.516	648	883	878	.5
4,900	.835	.393	493	669	667	.2
3,920	.603	.277	348	456	453	.3
2,940	.323	.147	184	243	235	.8
1,960	0.000	0.000	0.00000	0.00000	0.00014	— 1.4
PYRITE.						
$\Delta L_0 = -0.91$ $V = 20,163$ $Q = 0.33$ $10^4a = 0.8$ $10^6b = 0.710$						
7,840	0.131	0.061	0.00070	0.00424	0.00426	— .2
6,860	.109	.049	56	350	356	— .6
5,880	.100	.048	55	290	286	.4
4,900	.081	.039	45	221	217	.4
3,920	.057	.026	30	148	147	— .1
2,940	.037	.020	23	82	78	.4
1,960	0.000	0.000	0.00000	0.00000	0.00008	— .8



TABLE II.

*Experimental Results for Minerals in Granular Form. Volume of Reference Steel 10,674 (9879 for Diamond).*

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
-------------------------	------------	-----------------------	-------------------------------	--------------------------------	---------------------

## ACTINOLITE.

$$\Delta L_0 = 0.18 \quad V = 10,802 \quad V' = 9913 \quad V_{Cu} = 889 \quad Q = 0.52 \quad 10^4 a = 1.7 \quad 10^6 b = 1.320$$

12,000	0.199	0.312	0.01317	0.01337	-2.0
10,000	.167	.266	.1093	.1073	2.0
8,000	.117	.191	.818	.809	.9
6,000	.069	.131	.540	.545	-.5
4,000	.031	.067	.275	.281	-.6
3,000	.027	.047	.169	.149	2.0
2,000	0.000	0.000	0.00000	0.00017	-1.7

## AUGITE.

$$\Delta L_0 = 0.00 \quad V = 10,837 \quad V' = 9965 \quad V_{Cu} = 872 \quad Q = 0.665 \quad 10^4 a = 3.4 \quad 10^6 b = 1.035$$

12,000	0.106	0.206	0.01064	0.01069	-.5
10,000	.080	.169	.859	.862	-.3
8,000	.063	.137	.668	.655	1.3
6,000	.029	.085	.431	.448	-1.7
4,000	.025	.058	.252	.241	1.1
3,000	.030	.048	.171	.138	3.3
2,000	0.000	0.000	0.00000	0.00034	-3.4

## DIOPSIDE.

$$\Delta L_0 = 0.41 \quad V = 10,847 \quad V' = 9976 \quad V_{Cu} = 871 \quad Q = 0.69 \quad 10^4 a = 5.7 \quad 10^6 b = 1.089$$

12,000	0.063	0.237	0.01136	0.01146	-1.0
10,000	.046	.199	.928	.928	.0
8,000	.033	.161	.724	.710	1.4
6,000	.007	.104	.474	.493	-1.9
4,000	.020	.077	.297	.275	2.2
3,000	.038	.068	.217	.166	5.1
2,000	0.000	0.000	0.00000	0.00057	-5.7

## HYPERSTHENE.

$$\Delta L_0 = 0.40 \quad V = 10,675 \quad V' = 9901 \quad V_{Cu} = 774 \quad Q = -0.03 \quad 10^4 a = -0.2 \quad 10^6 b = 1.008$$

12,000	0.123	0.183	0.01022	0.01006	1.6
10,000	.082	.135	.789	.804	-1.5
8,000	.058	.102	.593	.603	-1.0
6,000	.040	.073	.407	.401	.6
4,000	.015	.035	.201	.200	.1
3,000	.006	.017	.99	.99	.0
2,000	0.000	0.000	0.00000	-0.00002	.2

## ENSTATITE.

$$\Delta L_0 = 0.30 \quad V = 10,688 \quad V' = 9910 \quad V_{Cu} = 778 \quad Q = 0.03 \quad 10^4 a = -0.4 \quad 10^6 b = 1.043$$

12,000	0.144	0.197	0.01054	0.01039	1.5
10,000	.101	.148	.819	.830	-1.1
8,000	.072	.111	.614	.622	-.8
6,000	.042	.071	.403	.413	-1.0
4,000	.024	.041	.215	.205	1.0
3,000	.008	.017	.99	.100	-.1
2,000	0.000	0.000	0.00000	-0.00004	.4



column 4 of Table II. The arbitrary initial pressure,  $P_0$ , is 2000 megabars: The values in the two columns mentioned therefore indicate, in  $\text{cm.}^3$ , how much one  $\text{cm.}^3$  (at 2000 megabars) of the material decreases in volume when the pressure is raised from 2000 megabars to the given pressure. It may be observed that this volume-change is nearly but not quite proportional to the pressure-

TABLE II.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
DIAMOND.					
$\Delta L_0=0.04$ $V=9080$ $V'=9891$ $V_{Cu}=811$ $Q=0.09$ $10^4a=-1.6$ $10^6b=0.180$					
12,000	-0.183	-0.166	0.00151	0.00164	-1.3
11,000	- .151	- .134	174	146	2.8
10,000	- .138	- .121	151	128	2.3
8,000	- .126	- .112	58	92	-3.4
6,000	- .089	- .078	30	56	-2.6
4,000	- .045	- .038	18	20	- .2
3,000	- .023	- .019	11	2	.9
2,000	0.000	0.000	0.00000	-0.00016	1.6

DIAMOND.					
$\Delta L_0=0.20$ $V=9080$ $V'=9891$ $V_{Cu}=811$ $Q=0.09$ $10^4a=-0.4$ $10^6b=0.205$					
12,000	-0.193	-0.151	0.00189	0.00201	-1.2
11,000	- .165	- .124	200	181	1.9
10,000	- .150	- .112	174	160	1.4
8,000	- .131	- .099	92	119	-2.7
6,000	- .084	- .061	74	78	- .4
4,000	- .042	- .027	46	37	.9
3,000	- .025	- .017	14	17	- .3
2,000	0.000	0.000	0.00000	-0.00004	.4

difference. As explained in a previous publication,<sup>24</sup> the volume-change as a function of pressure is represented by the equation :

$$-\frac{\Delta V_r}{V_r} = a + b(P - P_0) - c(P - P_0)^2$$

(3)

in which  $a$ ,  $b$ , and  $c$  are constants. The value of  $c$  is small in any case, and is zero when the volume-change is proportional to the pressure. For each series of measurements the coefficients,  $a$ ,  $b$ ,  $c$ , of equation (3) were calculated by the method of least squares; with these values of the coefficients, the values of  $-(\Delta V_r/V_r)$  were calculated from the equation and listed in column 6 of Table I and column 5 of Table II. How well the equation fits the data is shown by comparing the observed and calculated volume-changes. The differences between  $-(\Delta V_r/V_r)$  *obs.* and  $-(\Delta V_r/V_r)$  *calc.*

<sup>24</sup> Adams, Williamson, and Johnston, *op. cit.*, p. 36.



are shown in the last columns of Tables I and II. These differences average but little more than  $1 \times 10^{-4}$  and correspond to an average error of about 0.01 mm. in the measurement of piston-displacement. The error is greater with the granular material than with the cylinders, mainly because of the fact that less material could be used in the former case. The values of  $a$ ,  $b$ , and  $c$  for each series of measurements are included in Tables I and II. In those cases in which  $c$  is not given it is equal to zero.

TABLE III.  
*Summary of Results for Minerals.*

Mineral.	Composition.	Coeffs. of Eq. (4)		Compressibility, $\beta \times 10^6$		
		$b \times 10^6$	$c \times 10^{10}$	at 0	at 2000	at 10,000
Oligoclase . . . . .	$\text{Ab}_{78}.\text{An}_{22}$	1.712	0.083	1.74	1.71	1.58
Labradorite . . . .	$\text{Ab}_{48}.\text{An}_{52}$	1.508	0.109	1.55	1.51	1.34
(Anorthite)* . . . .	$\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$	.....	.....	....	(1.10)	(1.10)
(Andesine)* . . . .	$\text{Ab}_2.\text{An}_1$	.....	.....	....	(1.63)	(1.49)
(Labradorite)* . . .	$\text{Ab}_1.\text{An}_2$	.....	.....	....	(1.37)	(1.30)
(Albite)* . . . . .	$\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2$	.....	.....	....	(1.90)	(1.69)
Microcline . . . . .	$\text{Or}_{91}.\text{Ab}_9$	1.875	0.121	1.92	1.88	1.68
(Orthoclase) . . . .	$\text{K}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2$	.....	.....	(1.92)	(1.88)	(1.68)
Enstatite . . . . .	$(\text{MgSiO}_3)_{83}(\text{FeSiO}_3)_{12}$	1.031	.....	1.03	1.03	1.03
Hypersthene . . . .	$(\text{MgSiO}_3)_{70}(\text{FeSiO}_3)_{30}$	1.008	.....	1.01	1.01	1.01
Diopside . . . . .	$\text{CaO}.\text{MgO}.2\text{SiO}_2$	1.089	.....	1.09	1.09	1.09
Augite . . . . .	.....	1.035	.....	1.04	1.04	1.04
Actinolite . . . . .	.....	1.320	.....	1.32	1.32	1.32
Phlogopite Mica . .	.....	2.270	0.174	2.34	2.27	1.99
Pyrite . . . . .	$\text{FeS}_2$	0.710	.....	0.71	0.71	0.71
Diamond . . . . .	C	0.193	.....	0.18	0.18	0.18
[Quartz] † . . . . .	$\text{SiO}_2$	2.625	0.194	2.70	2.63	2.31
[Silica glass] † . . .	$\text{SiO}_2$	3.156	.....	3.1	3.1	....
[Calcite] † . . . . .	$\text{CaCO}_3$	1.390	.....	1.39	1.39	1.39
[Halite] † . . . . .	NaCl	4.006	0.295	4.12	4.01	3.53

\* By interpolation.

† Data from previous paper, Adams, Williamson and Johnston, *J. Am. Chem. Soc.*, 1919, 41, 39.

The experimental results for minerals are summarized in Table III, the third and fourth columns of which contain the weighted averages of  $b$  and  $c$ , respectively, for each of the minerals. Where more than one series of measurements was obtained for the same mineral, the average  $b$  was obtained by weighting the longer runs twice as much as the shorter ones; for  $c$  the ratio was 4 to 1. The coefficient,  $b$ , is equal to the compressibility,  $\beta$ , at  $P_0$  (2000 megabars), and the coefficient,  $c$ , is a measure of the change of compressibility with pressure. At any pressure the value of  $\beta$  may be obtained by differentiating equation (3); viz.,

$$\beta = b - 2c(P - P_0) \quad (4)$$



Table III shows the values of  $\beta$  at 0, 2000 and 10,000 megabars for the various minerals investigated, as obtained from  $b$  and  $c$  by means of equation (4). The compressibilities of albite and anorthite were obtained by graphical extrapolation of the values for oligoclase and labradorite, the assumption being made that for the plagioclase series the compressibility is a linear function of the composition<sup>25</sup> by volume (which in this case does not differ by an important amount from the composition by weight), and that the compressibility of anorthite is the same at 10,000 megabars as at 2000. The compressibility of diamond, according to the present measurements, is  $0.19 \times 10^{-6}$  per megabar, which agrees fairly well with the value,  $0.16 \times 10^{-6}$ , previously obtained by L. H. Adams<sup>26</sup> on somewhat less favorable material. The mean of these two determinations, rounded off to two significant figures, is  $0.18 \times 10^{-6}$ , and is thought to be the most probable value. The results of previous measurements,<sup>27</sup> carried out in this laboratory, on the three minerals, quartz, calcite, and halite, and on silica glass, are included in Table III.

From an inspection of Table III it may be seen that the compressibility of the minerals investigated varies from  $0.18 \times 10^{-6}$  for diamond up to  $4.12 \times 10^{-6}$  for halite (at  $P = 0$ ). Diamond, it may be mentioned, has the lowest compressibility of any known substance. As a rule, the higher the compressibility the more the change in compressibility with pressure. The compressibility of quartz, for example, falls off from  $2.70 \times 10^{-6}$  at  $P = 0$  to  $2.31 \times 10^{-6}$  at  $P = 10,000$ , a decrease of 14 per cent. for 10,000 megabars. Enstatite, on the other hand— $\beta = 1.03 \times 10^{-6}$ —shows, within the error of experiment, a constant compressibility over the whole pressure range. A dividing line can be drawn at  $\beta = 1.5 \times 10^{-6}$ , below which the compressibility changes so little as to escape detection by the present method, and above which the change of compressibility with pressure is easily measured. The single exception is silica glass which apparently shows constant compressibility— $\beta = 3.1 \times 10^{-6}$ —over the range of pressure used, which in that case was from 2000 to 8000 megabars.

The compressibility of the micropertite is almost identical with that of the albite, and since there is no reason to suppose that

---

<sup>25</sup> *Vide* Adams, Williamson, and Johnston, *op. cit.*, p. 40.

<sup>26</sup> *J. Wash. Acad. Sci.*, 1921, 11, 45-50.

<sup>27</sup> Adams, Williamson, and Johnston, *op. cit.*, p. 39.



microcline and orthoclase would differ in compressibility, the value assigned to the impure microcline in Table III, namely, 1.92, 1.88 and 1.68 at  $P = 0$ ,  $P = 2000$ , and  $P = 10,000$ , respectively, may be taken for the compressibility of pure orthoclase. Again, the compressibilities of the enstatite and of the hypersthene are practically the same—1.03 against 1.01—although the former contains (essentially) 12 per cent.  $\text{FeSiO}_3$  and the latter 30 per cent. The difference in compressibility is within the error of experiment; and therefore the compressibility of any mineral of the series, that is of any ordinary enstatite, bronzite, or hypersthene, is probably not far from  $1.02 \times 10^{-6}$ , the average of the above values.

It is an interesting and significant fact that the four pyroxenes investigated—enstatite, hypersthene, diopside, and augite—have compressibilities lying within a very narrow range, that is from  $1.01 \times 10^{-6}$  to  $1.09 \times 10^{-6}$ . They are less compressible than the amphibole, actinolite ( $\beta = 1.32 \times 10^{-6}$ ), and much less compressible than any of the feldspars except anorthite or anorthite-rich plagioclase. For a first approximation the compressibilities of the silicate minerals (pure  $\text{SiO}_2$  is excepted) may be calculated from certain values which may be assigned to the constituent oxides. These values, which may be called the “compressibilities in combination,” and which are not necessarily the same as the compressibilities of the actual oxides, are as follows:  $\text{SiO}_2$ , 1.4;  $\text{Al}_2\text{O}_3$ , 0.8;  $\text{FeO}$  (and  $\text{Fe}_2\text{O}_3$ ), 0.5;  $\text{MgO}$ , 0.7;  $\text{CaO}$ , 0.8;  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ , 6.0. The number of molecules (by weight) of each oxide is multiplied by the corresponding factor, and the sum of these products is divided by the total number of molecules.<sup>28</sup> The calculation agrees very closely with the observed values for all of the pyroxenes and the feldspars, but leads to too low a value for actinolite, probably on account of the water present in this mineral and on account of the inherently greater compressibility of the amphibole structure as compared with the pyroxene structure. A glance at the above list of factors for the various oxides shows the tremendous effect of soda and potash in increasing the compressibility of compounds.

By the use of the above factors the compressibility of the important mineral olivine is readily calculated to be  $0.93 \times 10^{-6}$ , and

<sup>28</sup> Probably greater accuracy could be attained by taking account of *molecular* volumes, and *molecular* compressibilities, of the oxides in combination, but there are insufficient data to justify such a calculation.



it is highly improbable that this value is in error by as much as 10 per cent.

*Rocks.*—The rocks were always investigated in the form of cylinders; granular material was not used, as was done in the case of some of the minerals. For the first group of experiments the cylinders were surrounded by kerosene and subjected to pressure just as the minerals were. In Table IV are given the experimental data including the volume-changes at each pressure as determined by the aid of equation (1). In this table the column headings and other symbols have the same significance as in Table I. The decrease of volume,  $-(\Delta V_r/V_r)$ , as before is nearly but not quite proportional to the increase of pressure,  $P - P_0$ , and follows equation (3) with sufficient accuracy. Rocks, unlike minerals, are usually porous; and before commenting on the compressibility of the rocks, we shall consider the effect of pressure on porous materials, and shall present the results of further experiments.

*Enclosed Rocks; "Inner" and "Outer" Compressibility.*—When a porous material, such as a rock, is in contact with the liquid which transmits the pressure, the liquid may penetrate the pores and act directly on the individual grains or non-porous parts of the solid. The compressibility then would be dependent mainly on the individual compressibilities of the constituents of the solid. The results of Table IV yield such a type of compressibility. According to the method of calculation used, the volume-change of the kerosene, whether outside the rock or within its pores, is eliminated, leaving for this set of data only the volume-change of the rock grains, and including no volume-decrease due to the packing together of the individual grains. This type of compressibility of a porous solid may be called its "*inner*" compressibility.

Now suppose that, on the other hand, the solid is covered by a thin, yielding, but impervious coating. The decrease in volume of the material when subjected to pressure would now include the effect of the packing together of the homogeneous parts of the solid—that is the effect of reduction in volume of the pore-space. As an example, consider the effect of pressure on a piece of sponge, (1) in contact with and surrounded by a liquid, and (2) also surrounded by the liquid, but covered with a close-fitting envelope of thin sheet rubber. The volume-change in the first case (assuming, of course, that the volume-change of the liquid is eliminated) is due entirely to the compressibility of the fibres of which the



TABLE IV.

*Experimental Results for Unenclosed Rocks. Volume of Reference Steel, 20,054.*

Pressure Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r$ $-\Delta V_s/V_s)$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
------------------------	------------	-----------------------	--	-------------------------------	--------------------------------	---------------------

## MARBLE.

$$\Delta L_0 = 0.08 \quad V = 20,078 \quad Q = -0.06 \quad 10^4 a = 1.8 \quad 10^6 b = 1.412$$

12,000	0.702	0.716	0.00826	0.01426	0.01430	— .4
11,000	.620	.632	729	1269	1289	— 2.0
10,000	.569	.580	670	1150	1147	.3
9,000	.510	.518	598	1018	1006	1.2
8,000	.435	.442	510	870	865	.5
7,000	.376	.381	440	740	724	1.6
6,000	.295	.297	343	583	583	.0
5,000	.226	.228	261	441	441	.0
4,000	.158	.160	185	305	300	.5
3,000	.089	.089	103	163	159	.4
2,000	0.000	0.000	0.00000	0.00000	0.00018	— 1.8

## MARBLE.

$$\Delta L_0 = 0.15 \quad V = 20,078 \quad Q = -0.06 \quad 10^4 a = 1.0 \quad 10^6 b = 1.410$$

7,840	0.389	0.404	0.00466	0.00820	0.00839	— 1.9
6,860	.338	.351	405	699	701	— .2
5,880	.277	.288	332	567	563	.4
4,900	.213	.221	255	431	425	.6
3,920	.146	.151	177	295	286	.9
2,940	.084	.086	99	158	148	1.0
1,960	0.000	0.000	0.00000	0.00000	0.00010	— 1.0

## SUDBURY DIABASE.

$$\Delta L_0 = -0.58 \quad V = 20,118 \quad Q = 0.15 \quad 10^4 a = 1.0 \quad 10^6 b = 1.237$$

12,000	0.632	0.570	0.00657	0.01257	0.01247	1.0
11,000	.560	.500	576	1116	1123	— .7
10,000	.505	.449	517	997	999	— .2
9,000	.449	.396	456	876	876	.0
8,000	.389	.341	393	753	752	.1
7,000	.327	.285	328	628	628	.0
6,000	.264	.227	262	502	505	— .3
5,000	.203	.173	199	379	381	— .2
4,000	.150	.129	148	268	257	.9
3,000	.084	.071	82	142	133	.9
2,000	0.000	0.000	0.00000	0.00000	0.00010	— 1.0

## SUDBURY DIABASE.

$$\Delta L_0 = -0.16 \quad V = 20,118 \quad Q = 0.15 \quad 10^4 a = -.9 \quad 10^6 b = 1.273$$

12,000	0.581	0.581	0.00668	0.01268	0.01264	.4
11,000	.514	.513	591	1131	1137	— .6
10,000	.461	.460	529	1009	1009	.0
9,000	.412	.410	472	892	882	1.0
8,000	.348	.346	398	758	755	.3
7,000	.288	.285	328	628	627	.1
6,000	.215	.213	245	485	500	— 1.5
5,000	.164	.162	186	366	373	— .7
4,000	.112	.111	128	248	246	.2
3,000	.051	.050	58	118	118	.0
2,000	0.000	0.000	0.00000	0.00000	— 0.00009	.9



TABLE IV.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r$ $-\Delta V_s/V_r)$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
PALISADE DIABASE.						
$\Delta L_0 = -0.40$ $V = 20,082$ $Q = -0.05$ $10^4a = 1.8$ $10^6b = 1.442$						
12,000	0.812	0.752	0.00867	0.01467	0.01460	.7
11,000	.716	.657	758	1298	1316	-1.8
10,000	.645	.589	679	1159	1171	-1.2
9,000	.579	.526	606	1026	1027	-.1
8,000	.511	.462	533	893	883	1.0
7,000	.431	.388	447	747	739	1.2
6,000	.348	.310	357	597	595	.2
5,000	.275	.244	281	461	451	1.0
4,000	.183	.160	184	304	306	-.2
3,000	.101	.089	103	163	162	.1
2,000	0.000	0.000	0.00000	0.00000	0.00018	-1.8
PALISADE DIABASE.						
$\Delta L_0 = 0.93$ $V = 20,082$ $Q = -0.05$ $10^4a = 1.5$ $10^6b = 1.428$						
12,000	0.567	0.713	0.00823	0.01423	0.01443	-2.0
11,000	.514	.652	752	1292	1300	-.8
10,000	.445	.572	660	1140	1157	-1.7
9,000	.413	.529	610	1030	1015	1.5
8,000	.361	.465	536	896	872	2.4
7,000	.298	.389	448	748	729	1.9
6,000	.234	.311	359	599	586	1.3
5,000	.181	.243	281	461	443	1.8
4,000	.105	.150	173	293	300	-.7
3,000	.044	.068	078	138	158	-2.0
2,000	0.000	0.000	0.00000	0.00000	0.00015	-1.5
PALISADE DIABASE.						
$\Delta L_0 = 0.80$ $V = 20,082$ $Q = -0.05$ $10^4a = 0.6$ $10^6b = 1.472$						
7,840	0.350	0.442	0.00511	0.00865	0.00872	-.7
6,860	.299	.381	440	734	728	.6
5,880	.231	.300	347	582	583	-.1
4,900	.175	.230	265	441	439	.2
3,920	.116	.157	181	299	295	.4
2,940	.060	.081	093	152	150	.2
1,960	0.000	0.000	0.00000	0.00000	0.00006	-.6
BASALT.						
$\Delta L_0 = 0.07$ $V = 20,097$ $Q = -0.05$ $10^4a = 0.8$ $10^6b = 1.895$ $10^{10}c = 0.214$						
12,000	0.922	0.939	0.01083	0.01683	0.01689	-.6
11,000	.858	.873	1007	1547	1540	.7
10,000	.778	.791	912	1392	1387	.5
9,000	.696	.707	816	1236	1230	.6
8,000	.591	.599	691	1051	1068	-1.7
7,000	.509	.515	594	894	903	-.9
6,000	.423	.428	494	734	732	.2
5,000	.331	.335	386	566	557	.9
4,000	.225	.227	256	376	378	-.2
3,000	.123	.125	144	204	196	.8
2,000	0.000	0.000	0.00000	0.00000	0.00008	-.8



TABLE IV.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ $-\Delta V_s/V_r$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
BASALT.						
$\Delta L_0 = 0.865$ $V = 20,097$ $Q = 0.05$ $10^4 a = 1.0$ $10^6 b = 1.852$ $10^{10} c = 0.196$						
7,840	0.471	0.571	0.00659	0.01013	0.01031	-1.8
6,860	.423	.509	588	882	871	1.1
5,880	.341	.415	479	714	706	.8
4,900	.258	.318	367	543	538	.5
3,920	.170	.214	247	365	366	— .1
2,940	.093	.116	134	193	190	.3
1,960	0.000	0.000	0.00000	0.00000	0.00010	-1.0
WESTERLY GRANITE.						
$\Delta L_0 = -0.47$ $V = 19,996$ $Q = -0.58$ $10^4 a = 1.0$ $10^6 b = 2.168$ $10^{10} c = 0.198$						
12,000	1.346	1.202	0.01393	0.01993	0.01980	1.3
11,000	1.216	1.078	1249	1789	1801	-1.2
10,000	1.108	0.976	1130	1610	1618	— .8
9,000	0.997	.875	1014	1434	1440	— .6
8,000	.870	.759	879	1239	1239	.0
7,000	.742	.642	743	1043	1044	— .1
6,000	.603	.517	600	840	845	— .5
5,000	.479	.409	474	654	643	1.1
4,000	.326	.275	318	438	436	.2
3,000	.176	.148	172	232	225	.7
2,000	0.000	0.000	0.00000	0.00000	0.00010	-1.0
WESTERLY GRANITE.						
$\Delta L_0 = 1.57$ $V = 19,996$ $Q = -0.58$ $10^4 a = 0.9$ $10^6 b = 2.064$ $10^{10} c = 0.139$						
7,840	0.573	0.700	0.00810	0.01164	0.01175	-1.1
6,860	.488	.598	693	987	989	— .2
5,880	.409	.502	581	816	797	1.9
4,900	.297	.372	431	607	604	.3
3,920	.188	.243	281	399	408	— .9
2,940	.110	.139	161	220	210	1.0
1,960	0.000	0.000	0.00000	0.00000	0.00009	— .9
STONE MOUNTAIN GRANITE.						
$\Delta L_0 = 0.67$ $V = 20,068$ $Q = -0.18$ $10^4 a = 1.0$ $10^6 b = 2.066$ $10^{10} c = 0.152$						
7,840	0.636	0.700	0.00809	0.01163	0.01173	-1.0
6,860	.550	.607	701	995	987	.8
5,880	.433	.480	554	789	796	— .7
4,900	.343	.381	440	616	604	1.2
3,920	.233	.260	301	419	410	.9
2,940	.117	.131	151	210	211	— .1
1,960	0.000	0.000	0.00000	0.00000	0.00010	-1.0
WASHINGTON GRANITE.						
$\Delta L_0 = -1.165$ $V = 20,021$ $Q = -0.44$ $10^4 a = 1.5$ $10^6 b = 2.240$ $10^{10} c = 0.248$						
7,840	0.936	0.760	0.00880	0.01234	0.01247	-1.3
6,860	.812	.655	758	1052	1053	— .1
5,880	.673	.538	624	859	855	.4
4,900	.540	.430	497	673	652	2.1
3,920	.365	.284	329	447	445	.2
2,940	.195	.152	176	235	232	.3
1,960	0.000	0.000	0.00000	0.00000	0.00015	-1.5



TABLE IV.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ $-\Delta V_s/V_r$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
OBSIDIAN.						
$\Delta L_0 = 0.51$ $V = 20,030$ $Q = -0.44$ $10^4a = -3.9$ $10^6b = 2.861$						
12,000	1.897	1.940	0.02243	0.02843	0.02822	2.1
11,000	1.691	1.728	1998	2538	2536	— .2
10,000	1.485	1.517	1754	2234	2250	— 1.6
9,000	1.307	1.344	1554	1974	1963	1.1
8,000	1.124	1.147	1326	1686	1677	.9
7,000	0.921	0.939	1086	1386	1391	— .5
6,000	.713	.726	841	1081	1105	— 2.4
5,000	.536	.546	632	812	819	— .7
4,000	.320	.326	378	498	533	— 3.5
3,000	.166	.170	197	257	247	1.0
2,000	0.000	0.000	0.00000	0.00000	— 0.00039	3.9
OBSIDIAN.						
$\Delta L_0 = 0.05$ $V = 20,030$ $Q = -0.44$ $10^4a = 0.5$ $10^6b = 2.857$						
7,840	1.190	1.158	0.01327	0.01681	0.01686	— .5
6,860	0.995	0.966	1117	1411	1405	.6
5,880	.799	.772	892	1127	1125	.2
4,900	.598	.575	665	841	845	— .4
3,920	.402	.384	444	562	565	— .3
2,940	.211	.201	233	292	285	.7
1,960	0.000	0.000	0.00000	0.00000	0.00005	— .5
SERPENTINE.						
$\Delta L_0 = -0.47$ $V = 20,122$ $Q = 0.08$ $10^4a = 0.9$ $10^6b = 1.819$ $10^{10}c = 0.301$						
12,000	0.860	0.808	0.00930	0.01530	0.01527	.3
11,000	.809	.760	875	1415	1402	1.3
10,000	.721	.673	775	1255	1271	— 1.6
9,000	.662	.617	712	1132	1135	— .3
8,000	.586	.542	624	984	992	— .8
7,000	.509	.473	546	846	843	.3
6,000	.423	.391	451	691	688	.3
5,000	.336	.309	356	536	528	.8
4,000	.234	.214	246	366	361	.5
3,000	.124	.113	130	190	188	.2
2,000	0.000	0.000	0.00000	0.00000	0.00009	— .9
SERPENTINE.						
$\Delta L_0 = 1.08$ $V = 20,122$ $Q = 0.08$ $10^4a = 0.4$ $10^6b = 1.675$ $10^{10}c = 0.124$						
7,840	0.363	0.502	0.00579	0.00933	0.00946	— 1.3
6,860	.317	.440	507	801	795	.6
5,880	.258	.362	418	653	642	1.1
4,900	.185	.269	310	486	486	.0
3,920	.119	.181	209	327	327	.0
2,940	.066	.092	106	165	167	— .2
1,960	0.000	0.000	0.00000	0.00000	0.00004	— .4



TABLE IV.—Continued.

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ $-\Delta V_s/V_r$	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
-------------------------	------------	-----------------------	--	-------------------------------	--------------------------------	---------------------

## PLATE GLASS.

$$\Delta L_0 = 0.49 \quad V = 20,148 \quad Q = 0.12 \quad 10^4 a = -0.1 \quad 10^6 b = 2.232 \quad 10^{10} c = 0.124$$

12,000	1.178	1.292	0.01487	0.02087	0.02107	-2.0
11,000	1.097	1.203	1385	1925	1907	1.8
10,000	0.968	1.066	1227	1707	1705	.2
9,000	.861	0.949	1092	1512	1500	1.2
8,000	.737	.816	939	1299	1294	.5
7,000	.601	.669	770	1070	1084	-1.4
6,000	.477	.533	614	854	872	-1.8
5,000	.378	.423	488	668	658	1.0
4,000	.237	.269	310	430	440	-1.0
3,000	.129	.147	169	229	221	.8
2,000	0.000	0.000	0.00000	0.00000	-0.00001	.1

## PLATE GLASS.

$$\Delta L_0 = 0.545 \quad V = 20,148 \quad Q = 0.12 \quad 10^4 a = 0.4 \quad 10^6 b = 2.215 \quad 10^{10} c = 0.054$$

7,840	0.718	0.803	0.00926	0.01280	0.01288	-.8
6,860	.615	.688	793	1087	1077	1.0
5,880	.484	.546	630	865	865	.0
4,900	.361	.410	472	648	651	-.3
3,920	.241	.276	318	436	436	.0
2,940	.124	.143	165	224	221	.3
1,960	0.000	0.000	0.00000	0.00000	0.00004	-.4

## CAST IRON.

$$\Delta L_0 = 0.20 \quad V = 20,008 \quad Q = -0.24 \quad 10^4 a = -0.6 \quad 10^6 b = 0.884 \quad 10^{10} c = 0.082$$

12,000	0.174	0.172	0.00199	0.00799	0.00796	.3
11,000	.150	.148	171	711	723	-1.2
10,000	.151	.150	173	653	649	.4
9,000	.139	.137	157	577	573	.4
8,000	.129	.127	147	507	495	1.2
7,000	.099	.097	112	412	416	-.4
6,000	.090	.089	103	343	334	.9
5,000	.050	.048	56	236	252	-1.6
4,000	.051	.049	57	177	168	.9
3,000	.012	.011	13	73	82	-.9
2,000	0.000	0.000	0.00000	0.00000	-0.00006	.6

## CAST IRON.

$$\Delta L_0 = 0.49 \quad V = 20,008 \quad Q = -0.24 \quad 10^4 a = 0.2 \quad 10^6 b = 0.889 \quad 10^{10} c = 0.096$$

12,000	0.117	0.162	0.00191	0.00791	0.00795	-.4
10,000	.117	.156	184	664	652	1.2
8,000	.080	.113	133	493	501	-.8
6,000	.062	.084	99	339	342	-.5
4,000	.038	.052	61	181	176	.5
3,000	.020	.027	32	92	90	.2
2,000	0.000	0.000	0.00000	0.00000	0.00002	-.2



sponge is composed, and is identical with the volume-change at the same pressure of a compacted piece of the same material. This corresponds to the inner compressibility. In the second case, however, the compressibility would be much greater; besides the change of volume of the fibres themselves there would be an additional effect due to the closing in of the pores. The compressibility in this case may be called the "*outer*" compressibility, which then refers to the total change in the volume as measured from the ordinary boundaries of the solid when pressure is exerted wholly from the outside and not at all through the pores of the material.<sup>29</sup> It is the outer compressibility which determines the volume-changes of rocks under pressure due to the weight of the overlying crust,<sup>30</sup> and which is comparable with the elastic constants obtained by indirect methods, *e.g.*, by loading a column and measuring the longitudinal contraction and the lateral extension.

The results listed in Table IV, yielding as they do merely the inner compressibility, are therefore not sufficient entirely to determine the effect of pressure on the volume of rocks. It would be difficult to predict in advance whether the effect of porosity would be large or small; measurements, under hydrostatic pressure, of the outer compressibility are required for the substances which are known to be porous. In order to accomplish this a new set of determinations was carried out on the rock cylinders after they had been enclosed in a jacket of thin sheet tin.

The method of enclosing the rocks was as follows: A close-fitting cylinder of pure tin,<sup>31</sup> about 0.1 mm. in thickness and about 2 mm. longer than the rock cylinders, was pushed over the rock and its ends turned over on to discs of tin which covered the ends of the rock. The rock with its covering was then heated in an oven to about 150° and the ends sealed by dipping momentarily into molten

---

<sup>29</sup> The difference between the inner and the outer compressibility is of course dependent only on the *open* pores; the *closed* pores would give an effect common to both methods of testing.

<sup>30</sup> We might distinguish a third kind of compressibility for porous solids in terms of the volume-change when the solid is enclosed in a thin envelope, but has its pores filled with liquid. The value of this compressibility would depend on the properties of the liquid, and would lie between the values for the inner and the outer compressibility.

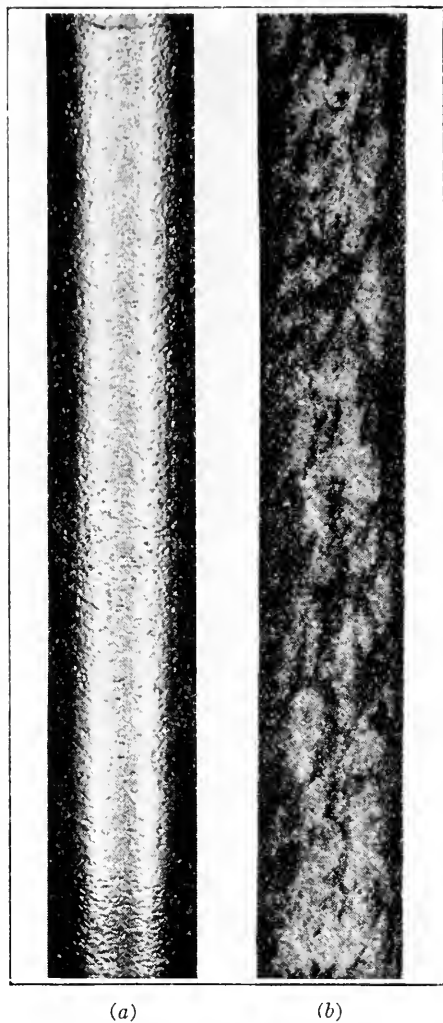
<sup>31</sup> Commercial tooth-paste tubes are very convenient for this purpose. To make them the correct size they can be enlarged a little by stretching them over a steel rod slightly tapered at one end.



solder which consisted of 37 per cent. lead and 63 per cent. tin and which was maintained at a temperature of about  $215^{\circ}$ .

Some difficulty was experienced at first in getting the covering sufficiently leak-proof so that kerosene at 12,000 megabars could not penetrate into the rock; but with care and patience it is possi-

FIG. 4.



Photograph of specimen of one rock (Washington granite), (a) covered with thin tin jacket, and (b) with the covering removed. (Natural size.)

ble to cover the rocks with a jacket which will keep out the kerosene and which at the same time is thin enough so that it can maintain only a small pressure difference, *i.e.*, so that the pressure is only a few megabars more than the pressure within the jacket. In order to ascertain whether or not the enclosure had held back the kerosene, the specimens were weighed before and after exposing them to pressure. If the weight was found to have increased, the



tin covering was taken off, the kerosene removed by heating in an oven and the cylinder enclosed again in a fresh tube. The appearance of cylinders after being subjected to pressure also served as an indication of whether or not the enclosure had held. If it had leaked, the surface of the tin usually remained smooth; but if there had been no leak, the surface took on a characteristic dimpled appearance—the tin had been forced so hard against the rock that it yielded a perfect replica in bright tin of the surface of the rock, the imperfections of which are more easily seen when copied in tin. (Fig. 4.)

In Table V are presented the results of the measurements on the enclosed rocks. The arrangement and symbols are similar to those of the preceding tables.  $V_{sn}$  is the volume of the tin enclosure,  $V'$  the volume of the rock, and  $V$  the total volume of the enclosed specimen—all at  $P=0$ . The values for the volume-change at a given pressure as shown in column 4 of this table are determined by the aid of equation (2) in which  $V_{sn}$  takes the place of  $V_{cu}$ . From these volume-changes, as before, are calculated the coefficients,  $a$ ,  $b$ , and  $c$  of equation (3), and finally the compressibility at the various pressures.

The change of volume caused by hydrostatic pressure is illustrated by Fig. 5, which shows graphically the results for two of the enclosed rocks. The decrease of volume per unit volume,  $-\Delta V/V$ , is plotted as ordinate, and the pressure,  $P$ , as abscissa. On a small scale, the lines appear very nearly straight, but the curvature for these two rocks actually is significant in amount, although much less than would be observed if the graph were extended to very low pressures—say two or three hundred megabars.

All of the results for rocks (and also for plate glass and cast iron) are summarized in Table VI. Four of the materials, namely, obsidian, serpentine, plate glass, and cast iron, are not porous and are absolutely impervious to kerosene under pressure; they were therefore not enclosed. The remaining eight rocks all show an appreciable porosity, an approximate value for which is given above in connection with the description of the materials. These rocks were investigated in the enclosed as well as in the unenclosed condition, except the gabbro, which was compressed only in the enclosed condition.



TABLE V.

*Experimental Results for Enclosed Rocks. Volume of Reference Steel 20,054 (18,516 for Marble, and 15,477 for Gabbro).*

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
-------------------------	------------	-----------------------	-------------------------------	--------------------------------	---------------------

## MARBLE.

$$\Delta L_0 = 0.69 \quad V = 18,528 \quad V' = 17,886 \quad V_{Sn} = 642 \quad Q = -0.09 \quad 10^4 a = 0.0 \quad 10^6 b = 1.387$$

12,000	0.560	0.668	0.01392	0.01387	.5
10,000	.436	.529	1106	1109	— .3
8,000	.316	.392	824	832	— .8
6,000	.212	.270	560	555	.5
4,000	.108	.140	298	277	.9
3,000	.044	.062	133	139	— .6
2,000	0	0	0	0	.0
1,000	—0.087	—0.112	—0.00196	—0.00139	—5.7

## SUDBURY DIABASE.

$$\Delta L_0 = 0.10 \quad V = 20,158 \quad V' = 19,492 \quad V_{Sn} = 666 \quad Q = 0.34 \quad 10^4 a = 0.1 \quad 10^6 b = 1.358$$

$$10^{10} c = 0.095$$

12,000	0.505	0.582	0.01266	0.01264	.2
10,000	.411	.478	1026	1027	— .1
8,000	.311	.366	783	782	.1
6,000	.211	.253	529	529	.0
4,000	.108	.131	270	269	.1
3,000	.056	.069	138	136	.2
2,000	0	0	0	1	— .1
1,000	—0.048	—0.056	—0.00124	—0.00136	1.2

## PALISADE DIABASE.

$$\Delta L_0 = 0.01 \quad V = 20,115 \quad V' = 19,361 \quad V_{Sn} = 754 \quad Q = 0.12 \quad 10^4 a = 1.0 \quad 10^6 b = 1.811$$

$$10^{10} c = 0.322$$

12,000	0.746	0.778	0.01505	0.01499	.6
10,000	.634	.659	1248	1253	— .5
8,000	.502	.522	969	981	— 1.2
6,000	.371	.385	691	683	.8
4,000	.203	.211	368	359	.9
3,000	.110	.114	194	188	.6
2,000	0	0	0	10	— 1.0
1,000	—0.106	—0.111	—0.00200	—0.00174	—2.6

## GABBRO.

$$\Delta L_0 = 0.57 \quad V = 15,489 \quad V' = 14,924 \quad V_{Sn} = 565 \quad Q = -0.03 \quad 10^4 a = -0.3 \quad 10^6 b = 1.347$$

$$10^{10} c = 0.123$$

12,000	0.289	0.383	0.01217	0.01221	— .4
10,000	.246	.328	1008	996	1.2
8,000	.176	.243	750	761	— 1.1
6,000	.125	.176	522	516	.6
4,000	.059	.087	260	261	— .1
3,000	.027	.042	128	130	— .2
2,000	0	0	0	3	.3
1,000	—0.054	—0.076	—0.00184	—0.00139	—4.5



TABLE V.—Continued.

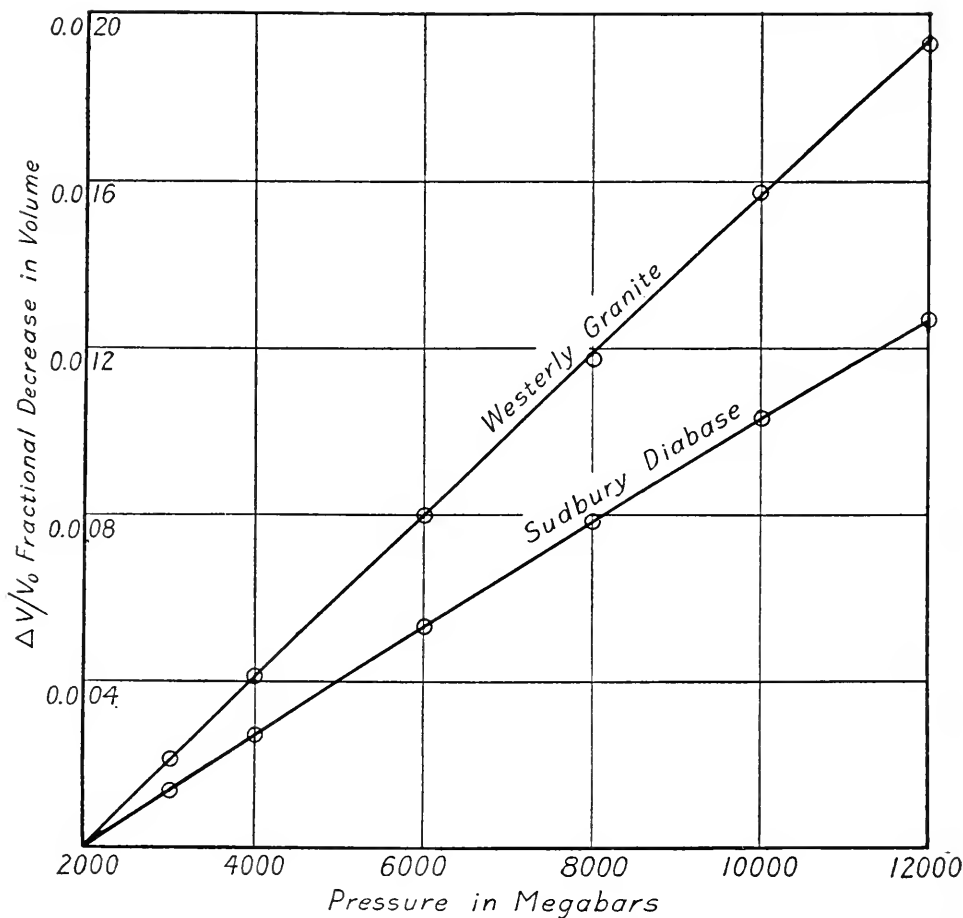
Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
BASALT.					
$\Delta L_0 = 1.09$ $V = 19,983$ $V' = 19,244$ $V_{Sn} = 739$ $Q = -0.52$ $10^4a = 1.2$ $10^6b = 2.431$ $10^{10}c = 0.455$					
12,000	1.122	1.226	0.01988	0.01988	.0
10,000	.953	1.051	1673	1666	.7
8,000	.744	.822	1295	1307	-1.2
6,000	.530	.588	910	912	-.2
4,000	.289	.321	486	480	.6
3,000	.160	.178	264	251	1.3
2,000	0	0	0	12	-1.2
1,000	-0.176	-0.199	-0.00288	-0.00236	-5.2
WESTERLY GRANITE.					
$\Delta L_0 = 1.01$ $V = 19,295$ $V' = 18,527$ $V_{Sn} = 768$ $Q = 3.47$ $10^4a = 0.2$ $10^6b = 2.010$ $10^{10}c = 0.076$					
12,000	1.405	1.060	0.01932	0.01936	-.4
10,000	1.181	.873	1577	1562	1.5
8,000	.903	.641	1164	1181	-1.7
6,000	.646	.444	797	794	.3
4,000	.349	.229	407	401	.6
3,000	.181	.113	201	202	-.1
2,000	0	0	0	2	-.2
1,000	-0.245	-0.148	-0.00250	-0.00200	-5.0
STONE MOUNTAIN GRANITE.					
$\Delta L_0 = 0.64$ $V = 20,131$ $V' = 19,530$ $V_{Sn} = 601$ $Q = 0.06$ $10^4a = 0.5$ $10^6b = 1.975$ $10^{10}c = 0.093$					
12,000	0.964	1.093	0.01886	0.01887	-.1
10,000	.785	.895	1533	1526	.7
8,000	.580	.670	1148	1157	-.9
6,000	.390	.456	776	780	-.4
4,000	.206	.244	408	396	1.2
3,000	.099	.120	201	202	-.1
2,000	0	0	0	5	-.5
1,000	-0.123	-0.152	-0.00240	-0.00193	-4.7
WASHINGTON GRANITE.					
$\Delta L_0 = 0.84$ $V = 19,383$ $V' = 18,741$ $V_{Sn} = 642$ $Q = -3.10$ $10^4a = 0.2$ $10^6b = 2.323$ $10^{10}c = 0.345$					
12,000	1.424	1.107	0.01980	0.01980	.0
10,000	1.214	.931	1639	1639	.0
8,000	.971	.731	1271	1271	.0
6,000	.692	.507	871	876	-.5
4,000	.383	.273	462	453	.9
3,000	.197	.135	228	231	.3
2,000	0	0	0	2	-.2
1,000	-0.222	-0.133	-0.00225	-0.00233	.8



TABLE V.—*Continued.*

Pressure (Megabars).	$\Delta L$	$\Delta L$ (corr.)	$-(\Delta V_r/V_r)$ (obs.)	$-(\Delta V_r/V_r)$ (calc.)	Diff. $\times 10^4$
WASHINGTON GRANITE.					
$\Delta L_0 = 1.01$ $V = 19,383$ $V' = 18,741$ $V_{Sn} = 642$ $Q = -3.10$ $10^4 a = -0.1$ $10^6 b = 2.255$ $10^{10} c = -0.293$					
12,000	1.378	1.090	0.01959	0.01961	— .2
10,000	1.179	.921	.1627	.1616	1.1
8,000	.925	.705	.1238	.1247	— .9
6,000	.664	.494	.855	.854	.1
4,000	.355	.254	.436	.438	— .2
3,000	.186	.129	.221	.222	— .1
2,000	0	0	0	1	.1
1,000	—0.205	—0.123	—0.00212	—0.00229	1.7

FIG. 5.



The decrease in volume of two of the materials investigated, at pressures from 2000 to 12,000 megabars. The observed points lie on smooth curves, which on the small scale of the diagram appear to be straight lines. Actually the curvature is appreciable.



TABLE VI.  
*Summary of Results for Rocks.\**

Material.	Coeffs. of Eq. (4)		Compressibility, $\beta \times 10^6$		
	$b \times 10^6$	$c \times 10^{10}$	at 0	at 2000	at 10,000
Marble unenclosed. ....	1.411	.....	....	1.41	1.41
Marble enclosed. ....	1.387	.....	....	1.39	1.39
Sudbury diabase unenclosed. ....	1.255	.....	....	1.26	1.26
Sudbury diabase enclosed. ....	1.358	0.095	....	1.36	1.21
Palisade diabase unenclosed. ....	1.442	.....	....	1.44	1.44
Palisade diabase enclosed. ....	1.811	0.322	....	1.81	1.30
Basalt unenclosed. ....	1.881	0.210	....	1.88	1.55
Basalt enclosed. ....	2.431	0.455	....	2.43	1.70
Gabbro enclosed. ....	1.347	0.123	....	1.35	1.15
Westerly granite unenclosed. ....	2.133	0.186	....	2.13	1.84
Westerly granite enclosed. ....	2.010	0.076	....	2.01	1.89
Stone Mt. granite unenclosed. ....	2.066	0.152	....	2.07	1.82
Stone Mt. granite enclosed. ....	1.975	0.093	....	1.98	1.83
Washington granite unenclosed. ....	2.240	0.248	....	2.24	1.84
Washington granite enclosed. ....	2.289	0.319	....	2.29	1.78
Obsidian. ....	2.860	.....	2.86	2.86	2.86
Serpentine (Talc Schist). ....	1.804	0.266	....	1.80	1.38
Plate glass. ....	2.226	0.110	2.27	2.23	2.05
(Cast iron). ....	0.887	0.089	....	0.89	0.76

\*The values for the enclosed rocks more truly represent the compressibilities of the materials.

COMPARISON WITH THE RESULTS OF EARLIER INVESTIGATORS.

*Minerals.*—A number of measurements on the compressibility of minerals have been made by Voigt<sup>32</sup> and by Madelung and Fuchs.<sup>33</sup> Voigt determined the elastic constants by bending and by twisting the crystals and measuring the deformation produced by a given stress. Madelung and Fuchs measured the compressibility under hydrostatic pressure, using a piezometer and working at a mean pressure of 125 megabars. For the sake of comparison some of the results of Madelung and Fuchs and all of Voigt's results are listed in Table VII. Voigt's values have been recalculated to correspond with our unit of pressure, the megabar. The results of Madelung and Fuchs with few exceptions are in good agreement with our measurements. Their value for silica glass is noticeably lower, and that for orthoclase is somewhat lower than the corresponding values obtained by us, but in the remaining cases where comparison is possible the agreement is excellent. Voigt's

<sup>32</sup> W. Voigt, *Ann. Physik*, 1887, 31, 474-501, 701-24; 1888, 34, 981-1028, 35, 642-61; 1890, 39, 412-31, 41, 712-24.  
<sup>33</sup> E. Madelung and R. Fuchs, *Ann. Physik*, 1921, 45, 289-309.



figures agree well in some cases, but for others they are much too high. But taking into consideration the difficulty of measuring the compressibility of crystals by an indirect method, the results of Voigt are, on the whole, surprisingly near the truth. The compressibilities of sylvite and halite have also been measured by Richards and Jones.<sup>34</sup> Their values, recalculated on the basis of the compressibility of mercury being  $3.96 \times 10^{-6}$  per megabar, are as follows:  $5.20 \times 10^{-6}$  for fused potassium chloride,

TABLE VII.

*Some Determinations of the Compressibility of Minerals by Other Investigators.*

Mineral.	Voigt $\beta \times 10^6$ (Pressure very low).	Madelung and Fuchs $\beta \times 10^6$ $P = 125$	A. & W. $\beta \times 10^5$ $P = 0$
Fluorite.....	1.18	1.24	....
Pyrite.....	1.13	0.71	0.71
Halite.....	4.13	4.13	4.12
Sylvin.....	7.37	5.62	....
Calcite.....	1.54	1.34	1.39
Tourmalin.....	1.15	0.84	....
Beryl.....	0.74	0.57	....
Quartz.....	2.65	2.66	2.70
Barite.....	1.92	1.76	....
Topaz.....	0.60	....	....
Magnetite.....	....	0.54	....
Corundum.....	....	0.41	....
Orthoclase.....	....	1.74	1.92
Silica glass.....	....	2.69	3.10
Magnesium oxide.....	....	0.71	....

$4.28 \times 10^{-6}$  for fused sodium chloride, and  $4.50 \times 10^{-6}$  for natural halite.

In connection with the compressibility of diamond it is interesting to note the value calculated by Thomson on the basis of his theory of the structure of solids.<sup>35</sup> For the compressibility of diamond the value obtained is  $0.18 \times 10^{-6}$ , in exact agreement with the mean of our measurements as given in Table III.

*Rocks.*—By measuring the longitudinal compression and the lateral extension under a unidirectional thrust, F. D. Adams and E. G. Coker<sup>36</sup> determined the compressibilities of a number of rocks and minerals. Their results, converted to the units used in

<sup>34</sup> T. W. Richards and Grinnell Jones, *J. Am. Chem. Soc.*, 1909, **31**, 158-91.

<sup>35</sup> J. J. Thomson, *Phil. Mag.*, 1922, **43**, 721-57.

<sup>36</sup> Carnegie Inst. Pub. No. 46.



this paper, are given in Table VIII. It is noticeable that, in the cases of substances used both by them and by us, there are considerable discrepancies except for plate glass and diabase. For instance, their values for cast iron and Westerly granite are 60

TABLE VIII.  
*Results of F. D. Adams and E. G. Coker at Low Pressures (Average about 300 Megabars); and, Where Comparison Is Possible, the Results of the Present Paper at the Lower End of Pressure Range—2000 Megabars.*

Material.	Compressi- bility, $\beta \times 10^6$ A. & C.	Compressi- bility, $\beta \times 10^6$ A. & W.	Remarks.
Wrought iron.....	0.68	0.60	Bessemer steel stand- ard of reference.
Cast iron.....	1.45	0.89	.....
Colorado marble.....	....	1.39	Identical with pure calcite (by direct method). All mar- bles at high pres- sures would give this result.
Black Belgian marble.....	1.74	....	.....
Carrara marble.....	2.44	....	.....
Vermont marble.....	2.72	....	.....
Tennessee marble.....	2.43	....	.....
Montreal limestone.....	2.35	....	.....
Baveno granite.....	3.15	....	.....
Peterhead granite.....	3.03	....	.....
Lily Lake granite.....	3.22	....	.....
Westerly granite.....	3.30	2.01	Sample cut from ma- terial furnished by A. & C. All granites practically same $\beta$ at high pressures.
Quincy granite (1).....	3.64	....	.....
Quincy granite (2).....	3.18	....	.....
Stanstead granite.....	3.68	....	.....
Stone Mountain granite.....	....	1.98	.....
Washington granite.....	....	2.29	.....
Nephelite syenite.....	2.33	....	.....
New Glasgow anorthosite.....	1.74	....	.....
Mount Johnson essexite.....	2.15	....	.....
New Glasgow gabbro (1).....	2.13	....	.....
New Glasgow gabbro (2).....	1.18	1.35	Sample from A. & C.
Sudbury diabase.....	1.36	1.36	Sample from A. & C.
Ohio sandstone.....	8.00	....	.....
Plate glass.....	2.25	2.23	.....

per cent. higher than ours, while an agreement to better than 1 per cent. is shown for the two previously mentioned substances.

There can be no doubt that the reason lies in the fact that, for the less compact materials, the bulk compressibility at low pressures changes rather rapidly with the pressure, and our experiments



began only at pressures considerably above the highest used by the others. If Hooke's law holds, in other words if the elasticity does not change with pressure, the change of volume produced by a unidirectional thrust is one-third that due to a hydrostatic pressure of the same intensity. But for substances whose compressibility changes with pressure there is a flaw in the assumption that the addition of two other equal thrusts at right angles to the first, so as to produce a total hydrostatic pressure, will each cause a change of volume equal to that produced by the first. If Hooke's law does not hold, more especially if the elastic properties are changing *rapidly* under pressure, the successive changes of volume will diminish so that the change of volume produced by the first will be greater than one-third of the total change, and compressibilities determined in this fashion will be too high.

If these ideas are correct, careful analysis of the results should show a decided change in the decrease of volume found by Adams and Coker for each increment of thrust. We have therefore calculated<sup>37</sup> and tabulated these values for the substances for which most experimental results are given. At each pressure the averages of the various measurements, of lateral extension and longitudinal contraction, were taken and the relative change of volume computed. In Table IX, these are compared with the values calculated from the equations.<sup>38</sup> In the cases of plate glass and diabase straight lines agreed sufficiently closely with the experimental data, but the differences in the case of the other substances justify the use of curves. Therefore the equations of the most probable

---

<sup>37</sup> In comparing compressibilities as determined by the two methods, (1) direct measurement under hydrostatic pressure, and (2) indirect determination from the deformation produced by a thrust, we must choose between two procedures: (a) The volume-change for a given unidirectional pressure is compared with the volume-change under a hydrostatic pressure equal to one-third of the unidirectional pressure; or (b) three times the volume-change produced by a given thrust is compared with the volume-change due to a hydrostatic pressure of the same intensity. In other words, the results of the indirect measurements of compressibility are recalculated (a) by dividing the pressures by 3, or (b) multiplying the volume-changes by 3. We have considered it more reasonable to adopt method (b) in comparing our values with those of Adams and Coker. The two procedures, (a) and (b), would yield identical results if the volume-changes were strictly proportional to the pressure, but when the compressibility changes with the pressure, procedure (a) would lead to a greater change of compressibility with pressure.

<sup>38</sup> Given at foot of Table IX.



parabolas to represent the data were calculated according to the same procedure as that used with our higher pressure results, and the values from those equations tabulated beside the observed values.

The compressibilities of plate glass and Sudbury diabase, 2.23 and 1.38, respectively, as calculated from these equations, agree as well as could be expected with the values obtained by Adams and Coker from the same data but by a different method of computa-

TABLE IX.

*Volume-changes Calculated from Results of Adams and Coker from Five Materials. For Plate Glass and Sudbury Diabase, the Relation of Volume-change to Pressure is Linear; for the Other Solids Curves Are Used.*

Pressure Mega- bars.	Plate glass.		Sudbury diabase.		Cast iron.		Westerly granite.		Sandstone.	
	$3 \times \frac{\Delta V}{V} \times 10^5$		$3 \times \frac{\Delta V}{V} \times 10^5$		$3 \times \frac{\Delta V}{V} \times 10^5$		$3 \times \frac{\Delta V}{V} \times 10^5$		$3 \times \frac{\Delta V}{V} \times 10^5$	
	obs.	from eqn.*	obs.	from eqn.†	obs.	from eqn.‡	obs.	from eqn.§	obs.	from eqn.¶
69	0	0	0	-2	0	-1	0	2	0	0
138	16	15	7	8	14	13	29	30	72	70
207	31	31	18	18	25	26	60	55	128	130
276	46	46	28	27	38	39	81	79	179	179
345	61	61	35	37	52	51	97	101	...	...
414	76	77	46	46	63	62	119	121	...	...
483	92	92	54	56	72	73	138	139	...	...
552	107	107	67	65	83	83	158	156	...	...
621	124	123	76	76	92	92	170	170	...	...

\* Plate glass.  $3 \times \frac{\Delta V}{V} \times 10^6 = 2.23 (P-69) - 3$ .

† Sudbury diabase.  $3 \times \frac{\Delta V}{V} \times 10^6 = 1.38 (P-69) - 15$ .

‡ Cast iron.  $3 \times \frac{\Delta V}{V} \times 10^6 = 2.04 (P-69) - 6.1 (P-69)^2 10^{-4} - 10$ .

§ Westerly granite.  $3 \times \frac{\Delta V}{V} \times 10^6 = 4.12 (P-69) - 19.6 (P-69)^2 10^{-4} + 20$ .

¶ Sandstone.  $3 \times \frac{\Delta V}{V} \times 10^6 = 10.9 (P-69) - 55 (P-69)^2 10^{-4}$ .

tion. The initial compressibilities of the other three substances come out higher, but the second term in the equation lowers the values rapidly at the higher pressures. The rate of change of the compressibility as shown by the second term is much greater than it is at higher pressures according to our results.

An equation to fit all the results, *i.e.*, those from 69 to 1200 megabars, may easily be constructed by the introduction of an exponential term. The following equations are suggested for the compressibilities :

Cast iron  $10^6\beta = 0.887 - 0.178(P-2000)10^{-4} + 0.022e^{-0.002(P-2000)}$  (5)

Westerly granite  $10^6\beta = 2.010 - 0.152(P-2000)10^{-4} + 0.006e^{-0.003(P-2000)}$  (6)



Above a pressure of 2000 megabars the exponential terms are negligible and these equations become simply those obtained from our high pressure results. At lower pressures the exponential term increases the value of  $\beta$  up to the values given by Adams and Coker's results, 2.12 and 4.46 at zero pressure. Integration shows that the effect of the exponential term is to add to the change of volume as calculated from the high pressure results a small amount (0.06 per cent. of the total volume for cast iron, and 0.08 per cent. for Westerly granite) which is due to some kind of packing effect at low pressures.

The elastic constants of rocks have also been measured by Nagaoka.<sup>39</sup> Specimens of the rocks were subjected to bending and to twisting, and the resultant deformations used to calculate Young's modulus  $E$  and the rigidity  $R$ . As has already been pointed out by Adams and Coker, the method used by Nagaoka when applied to rocks does not yield very satisfactory results—at least not for compressibility. In nearly every case the value of  $E$  given by Nagaoka is greater than three times  $R$ . Now, the relations between the elastic constants are such that when  $E/R$  is greater than 3, the compressibility must be negative—a situation which effectively bars any comparison between Nagaoka's results and ours.

The complete curves for the four substances, Sudbury diabase, Westerly granite, plate glass, and cast iron are plotted in Fig. 6. This diagram shows the course of the compressibility from zero to 12,000 megabars, and indicates how, for a given solid, a single curve may represent both the low-pressure results of Adams and Coker and the high-pressure results of the present paper.

#### DEPENDENCE OF COMPRESSIBILITY OF ROCKS ON VARIOUS FACTORS.

*Porosity and Compactness.*—It would naturally be expected that the compressibility of a rock would depend to a considerable extent on its porosity. That is, the "outer" compressibility should increase with the amount of pore space; the "inner" compressibility, of course, being unaffected, at least in the case of open pores. The effect of porosity may be judged first by the differences between these two compressibilities, and second by comparing the compressibilities at high pressures with those determined at low

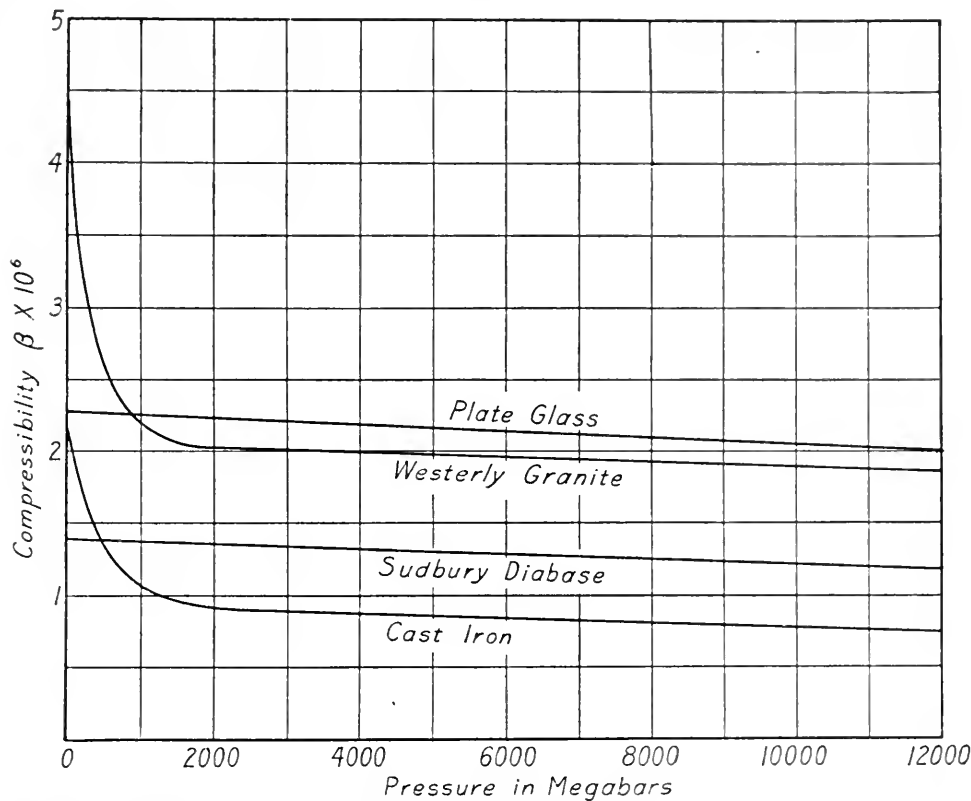
---

<sup>39</sup> H. Nagaoka, "Elastic Constants of Rocks and Velocity of Seismic Waves," *Phil. Mag.*, 1900, 50, 53-68.



pressures by Adams and Coker. By referring to Table VI it may be noted that the basalt and the Palisade diabase show a much higher compressibility when enclosed in the jacket of thin sheet tin than when unenclosed. The Sudbury diabase is somewhat more compressible, while the marble and the granites show very little difference, and in some cases appear to be actually less compressible in the enclosed condition. The differences, however, for the

FIG. 6.



The compressibility of four materials from 0 to 12,000 megabars. The values at low pressures were obtained from the data of F. D. Adams and E. G. Coker.

marble and the granites are hardly more than the experimental error.

The values with the enclosed rocks are to be regarded as the more accurate, principally because the volumes of the enclosed cylinders can be determined with greater precision. The enclosed Palisade diabase, while more compressible at low pressures than the unenclosed rock, appears to be slightly less compressible at high pressures. Possibly in this case the volume-change of the unenclosed rock, which was computed as a straight line, really follows a curve, so that the compressibility at low pressures is



higher and the compressibility at high pressures is lower than the mean,  $1.44 \times 10^{-6}$ , recorded in the table.

The compressibility of most granites and of some basic rocks seems to be considerably higher at very low pressures than at higher pressures. Moreover, the compressibility of one rock, the basalt, is notably greater in the enclosed condition than in the unenclosed condition, even at 2000 megabars. These differences might be thought to be due to the porosity of the rocks, but although porosity doubtless is a factor in determining the compressibility at low pressures, the relationship is not at all simple, and it is only when the exact distribution of the pore space is known that the effect on the measurements can be estimated with accuracy.

It will simplify the problem to consider certain particular cases of pore-distribution. Consider the effect of hydrostatic pressure on a number of spheres of the same external radius but with the following distributions of pore space: (*a*) No cavities; (*b*) a central spherical cavity the volume of which is 1 per cent. of the whole; (*c*) a large number of spherical cavities uniformly distributed, the total volume again being 1 per cent. of the whole; (*d*) a very narrow crack dividing a solid central sphere of half the total volume from an outer spherical shell comprising the remainder; and (*e*) a number of narrow cracks such as that considered in (*d*) but not completely spherical, and distributed throughout the mass. In case (*a*) the ordinary compressibility of the material is obtained. Cases (*b*) and (*c*) should show a compression a little over 2 per cent. more than (*a*). The same would be true of pores consisting of small channels ramifying through an otherwise sound material. In case (*d*) the initial compressibility will be that of the outer spherical shell and will be between two and three times as great as that of the solid sphere; but if the crack has a volume of only a few tenths of 1 per cent. of the total, it will close up completely when the pressure reaches a few hundred megabars, and at this pressure the compressibility will increase rapidly up to the normal value for the homogeneous material. Case (*e*) would show the same characteristics as (*d*) but the change in compressibility would be more gradual.

None of the rocks has enough porosity to explain, on the basis of detached voids or channels, more than a few per cent. increase



of compressibility. The Palisade diabase with less than 0.1 per cent. porosity shows an outer compressibility at 2000 megabars distinctly higher than the inner compressibility. The granites, moreover, although containing less than 1 per cent. of pore space, show an abnormally high compressibility at very low pressures: the value at a pressure of only a few hundred megabars being nearly double that at 1000 megabars. The total volume-change when Westerly granite is exposed to a pressure of 1000 megabars is only 0.3 per cent.; yet its compressibility at this pressure has fallen off to a much lower and nearly constant value.

It appears as if there were two main factors in causing the compressibility of some rocks to have an abnormally high value at low pressures. In the first place, there is probably a sort of looseness of structure,<sup>40</sup> or a lack of compactness in the rock. It is as if the mineral grains fit together rather loosely, and become tightly locked only after a certain amount of pressure is applied. Pores in the sense of small channels or detached voids would have very little effect; it is with relatively broad areas separating the grains that we have to deal (*cf.* case (*e*) above). The second factor is the combination of hard and soft (or rather, more compressible and less compressible) mineral grains in the same rock. The more compressible minerals themselves show a decreasing compressibility with increase of pressure, but this effect is relatively small. The granites, which as a class exhibit a very rapid drop in compressibility for the first few hundred megabars, consist of the highly compressible quartz and mica together with the less compressible feldspars. The case of cast iron is especially striking. Although it has no porosity, its compressibility decreases from about  $2 \times 10^{-6}$  at very low pressures to less than  $0.9 \times 10^{-6}$  at 2000 megabars. Here the admixture of the very compressible graphite and the very incompressible iron carbide is probably related to the initial rapid change in compressibility. On the other hand, marble consists of a single mineral and yet shows a large drop in compressibility, coming down to  $1.4 \times 10^{-6}$ , the value for calcite, at less than 2000 megabars. In this case the behavior can be ascribed only to that special

---

<sup>40</sup> The word structure is here used in its broadest sense.



kind of porosity connected with a looseness of assemblage of the mineral grains.<sup>41</sup>

Very often the abnormally high compressibility at low pressures is associated with coarseness of grain—for example, the granites and marbles, which are comparatively coarse-grained, show a high initial compressibility. The Sudbury diabase, however, is moderately coarse-grained and does not show much of this effect, while the serpentine, which is very fine-grained, shows a considerable decrease in compressibility and this tendency to decrease persists even at high pressures. For the latter substance the behavior is doubtless due to the admixture of the less compressible calcite with the more compressible talc. Palisade diabase also shows a considerable change of compressibility at high pressures, which is difficult to explain on any basis. It is fine-grained, almost non-porous, and consists largely of two minerals, augite and plagioclase ( $Ab_{40}An_{60}$ ) differing but little in compressibility.

About all that can be said concerning the way in which the compressibility of rocks changes with pressure is: For pressures above 2000 megabars the compressibility does not change very much; at pressures of only a few hundred megabars the compressibility is likely to be notably higher; and that the change of compressibility at low pressures, while connected with the admixture of minerals of different compressibility and with a looseness of structure existing in some coarse-grained rocks, can not with certainty be predicted in advance.

*Effect of Glass.*—The compressibility of a glass is probably always greater than that of a crystalline aggregate of the same chemical composition. The specific volume of the glass (with very few exceptions) is also higher, and it was thought at first that there might be a rough parallelism between volume and compressibility; but apparently no simple quantitative relation exists. Silica glass with 20 per cent. greater volume than quartz shows (at 2000 megabars) 15 per cent. greater compressibility, but on comparing the obsidian and the Westerly granite—which have nearly the same chemical composition—it may be noted that the obsidian with 10 per cent. greater volume has 40 per cent. greater compressibility. Possibly the difference in compressibility of these two

---

<sup>41</sup> The porosity and lack of compactness of the granites may, as has been suggested by various investigators, be due to the quartz-inversion, which takes place at 575° with a large change of volume.



forms of silica is small because the crystalline form itself has a comparatively high compressibility. As a rough estimate one can assume that for ordinary rocks the compressibility of the glassy material would be from one-fourth to one-third greater than that of the holocrystalline material of the same chemical composition.<sup>42</sup> The compressibility of two crystalline modifications of the same substance may, of course, differ, but usually not enough to destroy the utility of the suggested approximation for glasses.

*Relation of Rock-compressibility to That of the Constituent Minerals.*—The fact that the basic rocks have a low compressibility and consist of minerals of low compressibility, and that the

TABLE X.

*Comparison of the Observed Compressibility with the Values Calculated from the Compressibility of the Constituent Minerals.*

Rock.	Compressibility at 2000 megabars, $\beta \times 10^6$		Compressibility at 10,000 megabars, $\beta \times 10^6$	
	Observed.	Calculated.	Observed.	Calculated.
Westerly granite.....	2.01	2.09	1.89	1.86
Stone Mountain granite.....	1.98	2.04	1.83	1.81
Washington granite.....	2.29	2.06	1.78	1.85
Sudbury diabase.....	1.36	1.24	1.21	1.19
Palisade diabase.....	1.81	1.22	1.30	1.18
New Glasgow gabbro.....	1.35	1.08	1.15	1.06
Colorado marble.....	1.39	1.39	1.39	1.39

acid rocks have a much higher compressibility and consist of more compressible minerals suggests that the compressibility of a rock may be the average compressibility of the constituent minerals. This expectation has been fulfilled. Except at very low pressures, where the compressibility may be abnormally high, the compressibility of a rock can be calculated with fair accuracy from the known compressibility of its minerals. In Table X are shown the results of such calculation for seven holocrystalline rocks. The second column of this table contains the observed compressibilities copied from Table VI; the third column contains the compressibilities calculated from the modes, which are given above in connection with the description of the materials used. In the fourth and fifth columns are given the corresponding values at 10,000 megabars. To calculate the compressibility, the volume-percentage

<sup>42</sup> The problem is complicated by the fact that in partially crystalline rocks the vitreous part seldom has the composition of the rock as a whole.



of each mineral is multiplied by its compressibility; the sum of these products is then the "calculated" compressibility as shown in Table X. The compressibilities of the plagioclases for use in these calculations were interpolated from the values for albite and anorthite as given in Table III; the compressibilities of biotite and muscovite were assumed to be the same as for phlogopite; for that of epidote was taken the value for anorthite; and for that of olivine was taken 0.93, as estimated above (p. 494).

The observed and calculated values, on the whole, show a satisfactory agreement, especially so when the difficulty of accurately determining the mode is taken into account. The correspondence at 10,000 megabars is rather better than at 2000. The three granites are very close together as might be expected from the fact that the chief factor in yielding a high compressibility is quartz, which for the three granites varies only from 20 to 32 per cent. The Palisade diabase shows the greatest discrepancy between observed and calculated compressibility, while marble shows the least, the two values in this case being identical. The discrepancy for the Palisade diabase may possibly be connected with the presence of a saussuritized feldspar (included with plagioclase in the estimate of the mode). The rock is evidently not perfectly fresh, and the lessened compactness due to slight alteration would probably account for a higher compressibility especially at low pressures. A calculation for the basalt was not made because this rock contains a considerable amount of glass, the compressibility and composition of which is not known. The relatively high compressibility of the basalt, however, is another indication of the greater compressibility of a glass as compared with crystals of the same composition. The average discrepancy between observed and calculated compressibilities in Table X is 7 per cent., and neglecting the Palisade diabase the average is 5 per cent.

We thus come to the important conclusion that at moderately high pressures the compressibility of a fresh holocrystalline rock is an additive function of the compressibility of its minerals, provided that the pressure is not too low; in spite of considerable porosity, rocks at about 2000 megabars or more reach a compressibility which can be calculated from the mineral composition. But for certain rocks, notably the granites and probably also the other acid plutonic rocks, the compressibility below 1000 or 2000 megabars may be abnormally high. Thus, the compressibility of granite



may be above  $4 \times 10^{-6}$  at a pressure of 100 megabars—over twice as great as the compressibility at high pressures. On the other hand there are probably many rocks which maintain what we may call their normal compressibility down to very low pressures. An excellent example is the Sudbury diabase, which is a compact rock of low porosity. The compressibility, as shown by the measurements of Adams and Coker, is  $1.36 \times 10^{-6}$  at very low pressures, identical with our figure at 2000 megabars. For one specimen of the New Glasgow gabbro Adams obtained a lower value, and for another specimen a higher value, than ours. Here the relations are somewhat obscured by the obvious variability of the material, and indicate again the difficulty of predicting the compressibility of rocks at *very low* pressures.

The fact that the compressibility of rock masses can be calculated from the known compressibility of the constituent minerals is especially useful for the study of phenomena pertaining to those parts of the earth's crust which are not too near the surface. In the next section we proceed to make use of the relation between mineral- and rock-compressibility in listing certain elastic properties of a number of typical rocks.

#### ELASTIC CONSTANTS OF TYPICAL ROCKS.

The compressibilities of a number of types of plutonic igneous rocks have been calculated from the assumed mineral content, and the results are recorded in Table XI. The kind and amount of the minerals for each rock, as shown in the table, have been chosen so as to characterize the rock in terms of the essential constituents. The order of arrangement is that of increasing basicity, or decreasing percentage of silica. In order to round out the series, we include dunite, a massive igneous rock composed wholly of olivine; pallasite,<sup>43</sup> a mixture of iron and olivine composing certain meteorites although not found as a terrestrial surface rock; and also metallic iron. Siderite, a name used for meteorites composed wholly of metallic iron with a little nickel, is not to be confused with the terrestrial mineral siderite—ferrous carbonate.

The compressibility at two pressures (2000 and 10,000 megabars) is calculated from the compressibility of the constituent minerals according to the method already explained in connection

---

<sup>43</sup> Pallasite may be considered to consist, as a rough average, of about equal parts of olivine and metallic iron.



TABLE XI.

*Compressibility and Rigidity of Typical Plutonic Rocks at High Pressures; and the Velocity of Earthquake Waves as Determined by the Elastic Constants. The Compressibility is Calculated from the Compressibility of the Constituent Minerals, and the Rigidity is Computed by Assuming that at High Pressures Poisson's Ratio is 0.27.*

Rock.	Suggested Average Composition (by Volume).										Pressure Megabars.	Elastic Constants.			Density, <i>p.</i>	Velocity of Seismic Waves Km./sec.		Rock.
	Quartz.	Orthoclase.	Andesine. Ab <sub>2</sub> An <sub>1</sub>	Labradorite. Ab <sub>2</sub> An <sub>2</sub>	Biotite.	Amphibole.	Augite.	Hypersthene.	Olivine.	Metallic Iron.		Compressibility. <i>β</i> × 10 <sup>6</sup>	Bulk Modulus. <i>K</i> × 10 <sup>-6</sup>	Rigidity. <i>R</i> × 10 <sup>-6</sup>		Longitudinal. ( <i>L</i> ).	Transverse. ( <i>S</i> ).	
Granite.....	30	65	..	..	5	..	..	..	..	..	2,000	2.12	0.47	0.26	2.61	5.6	3.1	Granite
Granodiorite..	11	20	52	..	10	7	..	..	..	..	10,000 2,000	1.88 1.83	0.53 0.55	0.29 0.30	2.66 2.69	5.9 5.9	3.3 3.3	Granodiorite
Syenite.....	..	90	..	..	5	5	..	..	..	..	10,000 2,000	1.66 1.87	0.60 0.54	0.33 0.29	2.73 2.61	6.2 5.9	3.5 3.3	Syenite
Diorite.....	..	..	80	..	5	15	..	..	..	..	10,000 2,000	1.49 1.20	0.67 0.83	0.36 0.45	2.78 3.05	6.4 6.9	3.6 3.9	Diorite
Gabbro.....	..	..	..	50	..	..	40	10	..	..	10,000 2,000	1.17	0.85	0.46	3.08 3.40	6.9	3.9	Gabbro
Pyroxenite....	..	..	..	..	..	..	50	50	..	..	10,000 2,000	1.03	0.97	0.53	3.44 3.40	7.0	3.9	Pyroxenite
Peridotite....	..	..	..	..	..	..	..	50	50	..	10,000 2,000	0.97	1.03	0.56	3.44 3.38	7.2	4.0	Peridotite
Dunite.....	..	..	..	..	..	..	..	100	..	..	10,000 2,000	0.93	1.08	0.59	3.41 5.65	7.4	4.1	Dunite
Pallasite.....	..	..	..	..	..	..	..	50	50	..	10,000 2,000	0.77	1.30	0.71	5.69	6.3	3.5	Pallasite
Siderite.....	..	..	..	..	..	..	..	..	..	100	10,000	0.60	1.67	0.91	7.9	6.0	3.4	Siderite



with Table X. In the column adjoining the compressibilities are the corresponding values of the bulk modulus, which is obtained by taking the reciprocal of the compressibility. This quantity is of the same dimensions as pressure, *e.g.*, megabars, and is denoted by the letter  $K$ .

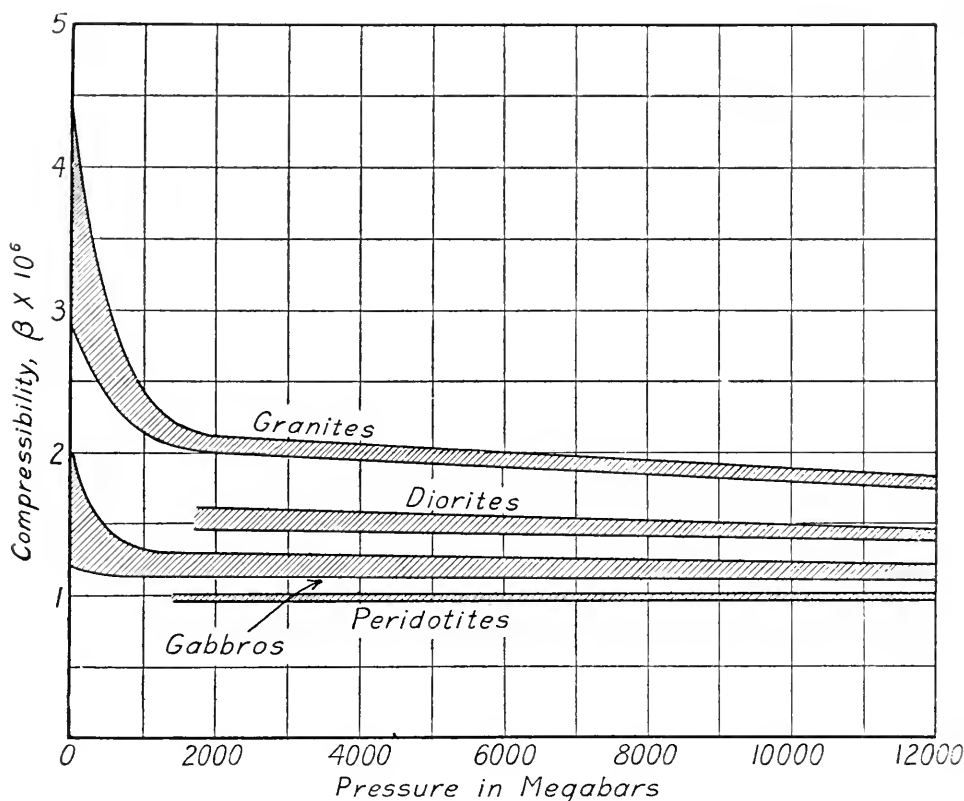
From a study of this table it may be seen that the compressibility decreases (and the bulk modulus, of course, increases) as we go down the list—except for syenite, which falls out of line. The more basic a rock, in general the less compressible it is. This may be considered a consequence of the inherently great compressibility of silica, even in combination, and also of the alkalis, which, as is well known, are more abundant in the acid rocks. Syenite, however, is an exception to the rule that the compressibility goes up as the silica goes down. Although the syenite has less silica than the granodiorite, its compressibility is greater. But it must be recalled that when rocks are arranged in order of basicity, syenite is to be considered a member of a branching series, and not a member of the main series in which quartz and orthoclase decrease together; in passing from granodiorite to syenite, the orthoclase increases while the quartz decreases. The same anomaly for syenite may be noticed in the case of the densities, which have been calculated from the densities of the minerals, and recorded in column 16. There is a progressive increase of density, except for syenite with its lower density than the granodiorite which it follows. If, however, we had chosen a granodiorite of slightly different composition, namely, quartz, 20; orthoclase, 25; andesine, 40; biotite, 10; and amphibole, 5, the compressibility of the granodiorite would have been sufficiently higher so that in Table XI the syenite would not have been an exception to the general rule of decreasing compressibility, as the rocks become more basic. But the densities of the granodiorites change so little for any reasonable range of composition that with respect to density syenite would still fall out of line.

It may be noted that the compressibility of the more acid rocks is a little less than that of plate glass ( $\beta = 2.2 \times 10^{-6}$ ), while that of the ultra-basic rocks (*e.g.*, a peridotite) is only about 50 per cent. greater than that of steel. The compressibilities of all ordinary rocks at moderate pressures lie between that of silver and that of plate glass.



Attention is called to the fact that although the compressibility of the more basic rocks appears to be constant throughout the pressure range from 2000 to 12,000 megabars, this is merely because the change in compressibility is too small to measure by the ordinary methods. With greater refinements of measurement, or with a greater range of pressure, there would undoubtedly be for all

FIG. 7.



The compressibility of four types of igneous rocks as a function of pressure. The width of the shaded areas indicates the variation which may be expected for ordinary rocks within the given class. At high pressures the variation is almost wholly due to the variation in composition; at low pressures, however, the range of variation is much larger and is dependent on the compactness of the rock.

substances a small but significant increase of bulk modulus, or decrease of compressibility, as the pressure is increased.

The compressibilities of four important rock types, granite, diorite, gabbro, and pyroxenite, are indicated in Fig. 7. The width of the shaded areas is intended to suggest the approximate variation in compressibility which may be expected to occur in the more common rocks of the given type. The assumed range of composition—which of course does not cover *all* rocks of the given type—is as follows: For the granites, from 30 to 15 per cent. quartz,



the biotite remaining constant at 5 per cent., and the remainder being orthoclase; for the diorites, from the composition given in Table XI to 40 per cent. andesine and 60 per cent. of amphibole; for the gabbros, from 25 to 75 per cent. labradorite, the remainder being augite; and for the pyroxenites, from 25 to 75 per cent. hypersthene, the remainder being olivine. The results of Adams and Coker, for six different granites, provide the basis for the estimate of the range of variation for the granites, at low pressures. The corresponding variation for the gabbros at low pressures is admittedly a very rough estimate representing mainly the opinion of the authors. The graphs for diorite and pyroxenite are not extended below 2000 megabars. It should be borne in mind that the variation at high pressures is almost entirely dependent on the composition of the rock, but at low pressures depends upon the compactness or state of aggregation as well as upon the composition.

In dealing with the elasticity of rock types, we take no account of extrusive rocks. It is to be noted, however, that such rocks if holocrystalline would have at high pressures the same elastic constants as intrusive rocks of the same composition; a rhyolite would not differ appreciably from a granite, unless it contained glass, nor, under the same conditions would an andesite differ from a diorite, nor a diabase from a gabbro. Moreover, we have little to say concerning the sedimentary or metamorphic rocks, but limit our discussion to the principal types of intrusives. This is partly because we have few experimental data for the former rocks, and also because, as a class, the igneous plutonic rocks constitute the greater part of the earth's crust.

*Rigidity.*—The rigidity is defined as the resistance to elastic deformation or change of shape; it is here denoted by the letter  $R$ , and like  $K$  is of the same dimensions as pressure, *e.g.*, megabars. If Poisson's ratio (the ratio of the lateral extension to the longitudinal contraction of a column subjected to a thrust) were known, the rigidity of a solid could be calculated from the bulk modulus by the well-known relation:

$$R = K \frac{3(1 - 2\sigma)}{2(1 + \sigma)} \quad (7)$$

$\sigma$  being Poisson's ratio. For highly elastic solids, that is for solids which to a high degree regain their original size and shape when stress is removed, the value of  $\sigma$  is generally assumed to



be about  $1/4$ . It is not unlikely that the plutonic rocks, which on the whole are compact, (essentially) isotropic, and highly elastic even at low pressures, may, especially at high hydrostatic pressures, fall into the class of substances for which  $\sigma$  is about  $1/4$ . A still more satisfactory estimate of the value of  $\sigma$  for rocks can be obtained directly from seismological data. From the ratio of the velocities at which the longitudinal and the transverse earthquake waves travel through the earth (*v. infra*) it may be seen that  $\sigma$  is nearly constant and equal to 0.27 for all depths.<sup>44</sup> It is interesting to note that for wrought iron (which in its elastic properties does not differ appreciably from steel) Poisson's ratio as determined by direct experiment<sup>45</sup> is about 0.28, and is thus very nearly the same as the value indicated for rocks. On the other hand, it must be admitted that at comparatively low pressures many rocks may show a somewhat smaller  $\sigma$ . For six different granites Adams and Coker<sup>45</sup> find the value of Poisson's ratio to vary from 0.20 to 0.26; but these are the very rocks which tend to show the greatest abnormality as regards change of compressibility at low pressures. The more basic rocks, which often maintain their high elasticity down to low pressures, are found by Adams and Coker to have a value of  $\sigma$  deviating very little from 0.26, except for one—presumably not isotropic—of the two specimens of New Glasgow gabbro.

But although there may be considerable variation in Poisson's ratio at very low pressures, there seems to be no reason to doubt that this factor for all rocks at moderate or high pressures is close to 0.27. Assuming this value for  $\sigma$ , we have from equation (7) :

$$R = 0.543 K = \frac{0.543}{\beta} \quad (8)$$

and the values of  $R$  in Table XI have been calculated in accordance with this relation.

The rigidity of the various rocks exhibits the same general trend as the bulk modulus; which follows, of course, from the fact that if  $\sigma$  is constant the two quantities except at very low pressures are simply proportional to each other. Both rigidity and

<sup>44</sup>  $\sigma = \frac{s^2 - 2}{2s^2 - 2}$ , where  $s$  is the ratio of the times required for the transverse and longitudinal waves, respectively, to reach a given point. Cf. K. Zoeppritz and L. Geiger, *Nachr. Gesell. Wiss. Göttingen. Math.-Phys. Klasse*, 1909, 4, 428.

<sup>45</sup> F. D. Adams and E. G. Coker, *op. cit.*, p. 69.



bulk modulus increase steadily with increasing basicity, except for the syenite, which, although following granodiorite, has a somewhat lower rigidity.

From the values here given it is evident that the rigidity of the more important formations of the earth's crust is considerably higher than has generally been supposed. This is especially the case when we confine our attention to pressures above 1000 megabars, that is to that part of the crust lying below 2 or 3 kilometres, and neglect the uppermost thin layer, where, particularly for the granites, the elasticity may be considerably smaller. The more compact basic rocks, however, may have nearly the same compressibility and rigidity at the surface as at lower levels. The rigidity of all ordinary igneous rocks is greater than that of plate glass; that of the granites is slightly larger, while that of a peridotite or pyroxenite is about twice as much as glass. The latter rocks have nearly two-thirds the rigidity of steel (or iron).

The average composition of surface rocks is, as noted above, practically identical with the granodiorite of Table XI. If we suppose that this same average composition persists to lower levels, the rigidity of the earth's crust would be about  $0.3 \times 10^6$  and its bulk modulus about  $0.6 \times 10^6$ . If, however, we incline to the view that the important part of the crust is largely gabbroic, the rigidity would be about  $0.5 \times 10^6$ .

It has long been known that the rigidity of the earth as a whole is remarkably high. At one time the rigidity was commonly stated to lie between that of glass and that of steel. Modern estimates, however, incline to the higher value. Thus Shida<sup>46</sup> states that the tidal deformation of the crust and the Chandler period of free nutation of the pole yield values close to  $1.2 \times 10^6$  megabars, while Michelson<sup>47</sup> obtains  $0.86 \times 10^6$ , almost exactly the rigidity of steel. No silicate rock can have so high a rigidity at pressures within the range of possible experimentation. The rigidity of the more basic rocks, however, is not much below the required amount, and would doubtless be notably higher at pressures corresponding to a depth of several hundred kilometres. The high rigidity of the earth finds its explanation, of course, in the fact that the value obtained by the various methods is a sort of average rigidity for the earth as a whole, and that the rigidity of the deeper parts of the

---

<sup>46</sup> T. Shida, *Mem. Coll. Sci. and Eng.*, 1912, 4, 116.

<sup>47</sup> A. A. Michelson, *Astrophys. Journ.*, 1914, 39, 105-38.



earth, whether silicious or metallic, is made higher by the enormous pressure at these great depths.

The increase of rigidity with increasing pressure is not to be confused with the increase of strength, that is the increased resistance to flow, which as shown by the measurements of Adams <sup>48</sup> is very considerable. These phenomena, while probably related, are separate and distinct effects.

It remains to discuss briefly the bearing of our values for the elastic constants of rocks on the propagation of earthquakes.

#### VELOCITY OF EARTHQUAKE WAVES.

The velocity at which seismic waves are transmitted through the earth is intimately connected with the elastic constants of the material of which the earth is composed. As is well known, there are two kinds of waves transmitted *through* the earth, one characterized by longitudinal vibrations and travelling with a velocity:

$$U_P \sqrt{\frac{K + \frac{4}{3}R}{\rho}} \quad (9)$$

and the other characterized by transverse vibrations travelling at a lower velocity, namely,

$$U_S \sqrt{\frac{R}{\rho}} \quad (10)$$

Here  $U$  is the velocity in cm./sec.,  $\rho$  is the density in g./cm.<sup>3</sup>, and  $K$  and  $R$  are to be taken in dynes/cm.<sup>2</sup>, that is  $10^6$  times the values given in megabars. Making use of the relation between  $R$  and  $\beta$  as given in equation (8), we have

$$U_P = \frac{13.13}{\sqrt{10^6 \beta \rho}} \quad (9a)$$

$$U_S = \frac{7.37}{\sqrt{10^6 \beta \rho}} \quad (10a)$$

in which  $\beta$  is now expressed in our customary unit, that is the reciprocal megabar, and  $U$  is in km./sec.

By means of equations (9a) and (10a) the velocities of the two kinds of earthquake waves for the typical igneous rocks were calculated and the results are shown in Table XI. The densities required for the calculation were computed for each rock from

<sup>48</sup> F. D. Adams, *J. Geol.*, 1912, 20, 97-118. See also L. King, *ibid.*, pp. 119-138.



the mineral densities by multiplying the volume-percentage of each mineral by the corresponding density and then adding these products together.

With increasing basicity the velocity of both waves increases (there being again a slight reversal at syenite) until the ultra-basic rocks are reached, but decreases on passing down the list to iron. The total variation in velocity is less than the variation in compressibility or rigidity because the velocity is proportional to the square root of the elasticity, and also because the greater density of the basic rocks partially compensates for their higher elasticity. The velocities are least for granite and greatest for dunite, the extreme values being 5.6 and 7.4 km./sec. for the fast wave, and 3.1 and 4.1 km./sec. for the slow one. The velocities of earthquake waves are known to vary with the distance from the source and hence with the depth to which the waves penetrate, and may be calculated from seismological data. The initial velocities, that is the velocities at or near the surface, are generally taken to be about 4 km./sec. for the transverse wave and a little above 7 km./sec. for the longitudinal one. These are the values corresponding to the pyroxenites or to the periodites, and are considerably above the velocities in the granitic rocks, although the velocity in granite as shown by Table XI is notably higher than had previously been supposed possible in rocks of that character. The results here given show the possibility of ascribing the high initial velocities of earthquakes to a preponderance of ultra-basic material at a comparatively small depth.

We shall not attempt at this time to discuss further the bearing of our results for the elastic constants of rocks on the question of the constitution of the earth. This subject will be taken up in a subsequent paper dealing with the earth's interior.

In conclusion we take this opportunity of acknowledging our indebtedness to Dr. Olaf Andersen, to Professor G. P. Merrill, to Mr. E. V. Shannon, and to Mr. Hans Brassler for furnishing us various mineral specimens; to Professor Frank D. Adams, who gave us specimens of several of the rocks with which he has worked; to Dr. H. E. Merwin and to Dr. N. L. Bowen for microscopical examination of many of the rocks and minerals; and to Dr. H. S. Washington for making seven complete chemical analyses for us, for the examination of many of the rocks and minerals, and for his kindly criticism and helpful suggestion.



## SUMMARY.

The compressibilities of a number of minerals and igneous rocks have been determined under hydrostatic pressures up to 12,000 megabars, corresponding to a depth of 40 kilometres below the surface of the earth. The method used has already been shown to yield consistent results for metals and other solids. According to this method the specimen is completely surrounded by a liquid, kerosene, and is subjected to pressure in a thick-walled steel bomb.

The compressibility of the minerals usually falls off slightly as the pressure is increased. For the less compressible minerals, however, the change in compressibility is so small as to escape detection by the present method, the precision of which corresponds to about  $0.01 \times 10^{-6}$  per megabar, that is to 1 per cent. of the total compressibility of the less compressible minerals. The absolute accuracy, of course, is not so high.

In connection with the compressibility of rocks, a complication is introduced by reason of their porosity, which even in igneous rocks is in many cases enough to affect the compressibility. In order to determine the effect of porosity at pressures within the range of experiment—1000 to 12,000 megabars—the porous rocks were covered with a thin jacket of pure tin, which served to prevent the liquid from entering the pores and thus allowed the closing-in of the pores to contribute to the decrease in volume of the sample as a whole. It was found that at pressures above 2000 megabars porosity has very little effect on the compressibility; but a comparison with the results of F. D. Adams and E. G. Coker shows that certain rocks, notably the more porous ones, may have at low pressures an abnormally high compressibility.

Our results show that except for very low pressures the compressibility of a rock may be calculated directly from the known compressibility of the constituent minerals, provided that the rock is holocrystalline. In general, the compressibility increases with increasing basicity, that is with decreasing silica content. Quartz and metallic iron may be considered to stand at the two extremes as regards the compressibility of igneous rocks. In any given class of rocks the variation in compressibility at high pressures is small and almost wholly due to the variation in composition; at low pressures the variation from one rock to another in the same class is much larger and depends mainly on the degree of compactness of



the rock. The granites as a rule show at low pressures a compressibility much above what may be called the normal compressibility, but basic rocks may preserve their relatively small normal compressibility down to low pressures. At 10,000 megabars the compressibility of a typical granite is about  $1.9 \times 10^{-6}$  per megabar, and that of a typical gabbro is about  $1.2 \times 10^{-6}$ .

From the ratio of the velocities of the two kinds of waves transmitted through the earth and from the known elastic behavior of compact rocks, it is believed that the value of Poisson's ratio for rocks at moderate or high pressures is very close to 0.27. From this value and from the measured compressibility the rigidity of a number of typical rocks is calculated. The rigidity of a typical granite at 10,000 megabars is  $0.3 \times 10^6$  megabars; that of a typical gabbro is  $0.5 \times 10^6$ ; and that of an ultra-basic rock, *e.g.*, a dunite, is  $0.6 \times 10^6$ . The rigidity of the earth as a whole, which is probably near that of steel ( $0.9 \times 10^6$ ), is higher than the value for the most rigid silicate rock, but doubtless the rigidity of a basic or ultra-basic rock is raised enough by a pressure corresponding to a few hundred miles of rock to yield the required value.

From the values of the bulk modulus (the reciprocal of the compressibility) and of the rigidity the velocities of the two kinds of waves transmitted through the earth are calculated for the various types of rocks. With increasing basicity of the rocks the velocity of the longitudinal vibrations increases steadily from the value for granite, 5.6 km./sec., to that for dunite, 7.4 km./sec., but is lower, 6.0 km./sec., for metallic iron. The initial velocity of the longitudinal vibrations is usually taken to be a little above 7 km./sec. This corresponds to a gabbro or to a pyroxenite, and furnishes an indication of basic or ultra-basic material at a relatively small depth below the surface of the earth.

---

**The Mechanics of Newton Versus the Mechanics of Einstein.**  
J. LEROUX. (*Comptes Rendus*, Dec. 26, 1922.)—"Most of the discussions of the principle of Einstein are vitiated by a fundamental error which should be dissipated, *viz.*, that the mechanical system of Newton is an approximation to that of Einstein. The two theories rest on entirely different principles. They give results almost alike in the case of a single moving body, but no one has the right to draw the conclusion that their consequences are always close together for systems of bodies. An affirmation of this kind is as false as a statement claiming that two curves near to each other in a limited region are constantly near together throughout their entire extent."



**A Critical Review of Trouton's Law, and its Applicability to the Triple Point.** SASI BHUSAN MALI. (*Phil. Mag.*, Jan., 1923.)—"The generalized Trouton law may be expressed by saying that the latent heat of change of state of a substance is proportional to the temperature of change of state, and the ratio of the two is approximately the same for all substances, provided the same kind of change of state is involved." Nernst found that this did not hold generally for vaporization. The author tries to find some circumstances under which the law is true. It certainly does not hold in the case of water for which there is no proportionality between the two quantities, temperature and latent heat, unless 40 and 16 are to be regarded as alike. When the ratio is examined for corresponding states of substances no theoretical basis of the law can be found. The author tries the triple point, but again here a wide divergence of ratios comes to light, so that he is forced to conclude, "It thus seems fairly well established that there is no particular point of temperature at which the Trouton law holds. Neither does the law seem to have any theoretical significance." G. F. S.

**Relative Visibility of Spectra When an Electric Discharge is Passed through the Vapors of Alkali Amalgams.** F. H. NEWMAN. (*Phil. Mag.*, Jan., 1923.)—Amalgams of sodium, potassium, lithium, rubidium and cesium, all were used. "At 100° C., the mercury lines predominate, but at 200° C. the spectra of the alkali metals are brighter than the mercury spectrum. The sodium D-lines mask the mercury lines at the higher temperature. The potassium spectrum is very faint under all conditions. The employment of the amalgams of the alkali metals, instead of the latter, forms a useful and convenient method for obtaining the spectra of the alkali metals. A brilliant D-line radiation is obtained with sodium amalgam." Two factors are concerned in determining the relative intensities of the spectra of the two elements present, their respective ionization potentials and their vapor-pressures. For instance, the ionizing potential of mercury is higher than that of sodium and yet it is the mercury spectrum that predominates at the lower temperature.

"At low temperatures, although the vapor-pressure of mercury is large compared with that of sodium, the actual values in both cases are small. As a result, the sodium atoms in the discharge-tube will be comparatively few. The mercury atoms also will probably be so far apart that the electrons attain the energy necessary to ionize the mercury atoms before they collide inelastically with any of the atoms. At low vapor-pressures, therefore, it is probable that the same proportion of mercury and sodium atoms present in the tube will be ionized. The intensity of the radiation emitted must be intimately connected with the concentration of the radiating atoms in the source, so that as the concentration of the radiating mercury atoms is greater than that of the sodium, we should expect the mercury lines to predominate." G. F. S.



# A SURVEY OF EXISTING CRYSTAL STRUCTURE DATA.\*†

BY

RALPH W. G. WYCKOFF, Ph.D.

Physical Chemist, Geophysical Laboratory, Carnegie Institution of Washington.

## DOUBLE HALIDES AND CYANIDES.

### DOUBLE CYANIDES OF DI- AND UNIVALENT ELEMENTS.—

The crystal structures have been studied<sup>122</sup> of cubic cyanides of the type  $K_2R(CN)_4$ , where R is either zinc, cadmium or mercury. The coördinate positions of the atoms within the unit cube which contains eight chemical molecules (Fig. 18) have been established from spectrographic and Laue photographic data to be:

Potassium:  $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ ;  $\frac{7}{8}\frac{1}{8}\frac{1}{8}$ ;  $\frac{3}{8}\frac{7}{8}\frac{1}{8}$ ;  $\frac{5}{8}\frac{5}{8}\frac{3}{8}$ ;  
 $\frac{1}{8}\frac{5}{8}\frac{1}{8}$ ;  $\frac{1}{8}\frac{1}{8}\frac{5}{8}$ ;  $\frac{5}{8}\frac{1}{8}\frac{5}{8}$ ;  $\frac{5}{8}\frac{5}{8}\frac{5}{8}$ ;  
 $\frac{7}{8}\frac{3}{8}\frac{1}{8}$ ;  $\frac{1}{8}\frac{7}{8}\frac{3}{8}$ ;  $\frac{3}{8}\frac{7}{8}\frac{3}{8}$ ;  $\frac{5}{8}\frac{3}{8}\frac{3}{8}$ ;  
 $\frac{7}{8}\frac{5}{8}\frac{7}{8}$ ;  $\frac{7}{8}\frac{5}{8}\frac{5}{8}$ ;  $\frac{5}{8}\frac{7}{8}\frac{7}{8}$ ;  $\frac{3}{8}\frac{3}{8}\frac{5}{8}$ .

Divalent metal atom:  $000$ ;  $\frac{1}{2}\frac{1}{2}0$ ;  $0\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ ;  $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ .

Carbon:  $uuu$ ;  $u + \frac{1}{2}, u + \frac{1}{2}, u$ ;  $u + \frac{1}{2}, u, u + \frac{1}{2}$ ;  $u, u + \frac{1}{2}, u + \frac{1}{2}$ ;  
 $u\bar{u}\bar{u}$ ;  $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$ ;  $u + \frac{1}{2}, \bar{u}, \frac{1}{2} - u$ ;  $u, \frac{1}{2} - u, \frac{1}{2} - u$ ;  
 $\bar{u}u\bar{u}$ ;  $\frac{1}{2} - u, u + \frac{1}{2}, \bar{u}$ ;  $\frac{1}{2} - u, u, \frac{1}{2} - u$ ;  $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$ ;  
 $\bar{u}\bar{u}u$ ;  $\frac{1}{2} - u, \frac{1}{2} - u, u$ ;  $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$ ;  $\bar{u}, \frac{1}{2} - u, u + \frac{1}{2}$ ;

$\frac{1}{4} - u, \frac{1}{4} - u, \frac{1}{4} - u$ ;  $\frac{3}{4} - u, \frac{3}{4} - u, \frac{1}{4} - u$ ;  $\frac{3}{4} - u, \frac{1}{4} - u, \frac{3}{4} - u$ ;  $\frac{1}{4} - u, \frac{3}{4} - u, \frac{3}{4} - u$ ;  
 $\frac{1}{4} - u, u + \frac{1}{4}, u + \frac{1}{4}$ ;  $\frac{3}{4} - u, u + \frac{3}{4}, u + \frac{1}{4}$ ;  $\frac{3}{4} - u, u + \frac{1}{4}, u + \frac{3}{4}$ ;  $\frac{1}{4} - u, u + \frac{3}{4}, u + \frac{3}{4}$ ;  
 $u + \frac{1}{4}, \frac{1}{4} - u, u + \frac{1}{4}$ ;  $u + \frac{3}{4}, \frac{3}{4} - u, u + \frac{1}{4}$ ;  $u + \frac{3}{4}, \frac{1}{4} - u, u + \frac{3}{4}$ ;  $u + \frac{1}{4}, \frac{3}{4} - u, u + \frac{3}{4}$ ;  
 $u + \frac{1}{4}, u + \frac{1}{4}, \frac{1}{4} - u$ ;  $u + \frac{3}{4}, u + \frac{3}{4}, \frac{1}{4} - u$ ;  $u + \frac{3}{4}, u + \frac{1}{4}, \frac{3}{4} - u$ ;  $u + \frac{1}{4}, u + \frac{3}{4}, \frac{3}{4} - u$ .

Nitrogen: a similar set of positions in  $v$ .

For the zinc salt the position of the centre of the cyanide group lies close to  $\frac{1}{2}$  ( $u + v$ ) = 0.37. The data from the other two salts are in harmony with this result, but are of a much scantier nature. With these two variable parameters and the present lack of knowledge concerning scattering, it was not possible to determine with certainty the exact positions of the nitrogen and carbon atoms. For the double zinc cyanide, however, the data accord best with one atom at about 0.34 and the other at 0.40.

*Potassium Zinc Cyanide*,  $K_2Zn(CN)_4$ .—The length<sup>122</sup> of the side of the unit cube is found to be:  $a = 12.54$  A.U.

*Potassium Cadmium Cyanide*,  $K_2Cd(CN)_4$ .—The length<sup>122</sup> of the side of the unit cube is:  $a = 12.84$  A.U.

\* Communicated by Dr. Arthur L. Day, Director of the Geophysical Laboratory and Associate Editor of this JOURNAL.

† Concluded from JOUR. FRANK. INST., March, 1923, 195, No. 3. p. 365.



*Potassium Mercury Cyanide*,  $K_2Hg(CN)_4$ .—The length <sup>122</sup> of the side of the unit cube:  $a = 12.76A.U.$

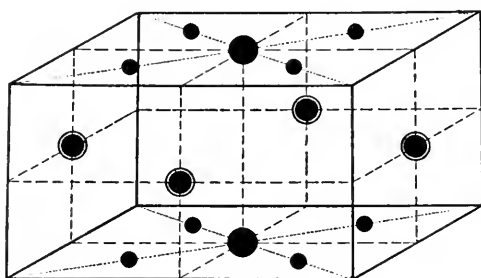
DOUBLE HALIDES OF DI- AND UNIVALENT ELEMENTS.—Studies have been made of tetragonal crystals of the type  $R_2XCl_4$ , where R is ammonium or potassium and X is platinum or palladium. The following arrangement (Fig. 19) was found to be the simplest which would account for spectrum and Laue photographic data.<sup>101</sup>

Potassium or Nitrogen:	$0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$ .
Platinum or Palladium:	000.
Chlorine:	$uuo; \bar{u}u0; u\bar{u}0; \bar{u}\bar{u}0$ .

For each crystal examined  $u$  has been found to be close to 0.23.

*Potassium Chloroplatinite*,  $K_2PtCl_4$ .—The dimensions <sup>101</sup> of

FIG. 19.



The arrangement of the atoms within the unit tetragonal prism assigned to potassium chloroplatinite. Platinum atoms are shown by large, chlorine by small black circles.

the unit prism described above are found to be:  $a = 6.99A.U.$ ,  $c = 4.13A.U.$

*Potassium Chloropalladite*,  $K_2PdCl_4$ .—The dimensions <sup>101</sup> of the unit prism are:  $a = 7.04A.U.$ ,  $c = 4.10A.U.$

*Ammonium Chloropalladite*,  $(NH_4)_2PdCl_4$ .—The dimensions <sup>101</sup> of the unit prism are:  $a = 7.21A.U.$ ,  $c = 4.26A.U.$

DOUBLE HALIDES OF QUADRI- AND UNIVALENT ELEMENTS.—The structures of the cubic crystals ammonium chloroplatinate, potassium and ammonium chlorostannates and ammonium fluosilicate have been studied. It is conclusively shown <sup>123, 124</sup> that these isomorphous compounds have the following arrangement of their atoms within the unit cube (Fig. 16).

Quadrivalent atoms:  $000; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$ .

Univalent metal atoms (or nitrogen atom of an ammonium group):

$\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}$ .



Halogen atoms: The same twenty-four equivalent positions that have defined the positions of the nitrogen atoms in hexammonates of the nickel halides (see March issue, page 363).

Hydrogen atoms: The thirty-two equivalent hydrogen atoms within the unit cell of the ammonium compounds will presumably have the arrangement that has been designated<sup>123</sup> as 32a. Their positions cannot, however, be determined from the diffraction data. It has also been reported<sup>119</sup> that potassium chloroplatinate has this same structure.

*Potassium Chloroplatinate*,  $K_2PtCl_6$ .—No data have yet been published.<sup>119</sup> Apparently upon the basis of powder measurements  $u$  has been given a value around 0.16. This parameter is the same in the ammonium and potassium chlorostannates,<sup>124</sup> and it is probable that the ammonium and potassium chloroplatinates are similar. Inasmuch as a complete study<sup>123</sup> of the structure of the ammonium salt has shown that  $u = \pm 0.24$ ,  $u$  for the potassium chloroplatinate may be expected to be near to 0.24. A further investigation is consequently to be desired.

*Ammonium Chloroplatinate*,  $(NH_4)_2PtCl_6$ .—The value<sup>123</sup> of  $u$  for chlorine lies between 0.22 and 0.24. The length of the side of the unit cube is given as:  $a = 9.84A.U.$

*Potassium Chlorostannate*,  $K_2SnCl_6$ .—The chlorine parameter<sup>124</sup> must be less than 0.25 and lie close to 0.245. The length of the side of the unit cube is given as:  $a = 9.99A.U.$

*Ammonium Chlorostannate*,  $(NH_4)_2SnCl_6$ .—The parameter<sup>124</sup>  $u$  is the same (around 0.245) as for the potassium salt. The length of the side of the unit cube is likewise almost the same:  $a = 10.05A.U.$

*Ammonium Fluosilicate*,  $(NH_4)_2SiF_6$ .—This crystal is dimorphous, one form being cubic, the other hexagonal. Only the former has been investigated.<sup>125</sup> It is concluded that  $u$  is close to 0.205. The length of the side of the unit cube is determined to be:  $a = 8.38A.U.$

SUMMARY OF THE STRUCTURES OF SIMPLE AND COMPLEX HALIDES, CYANIDES, ETC.—The structures of the crystals of this group that have been studied are summarized in Table IV.

#### NITRATES, CHLORATES, BROMATES.

*Sodium Nitrate*,  $NaNO_3$ .—Neither of the two investigations<sup>86, 126</sup> of the structure of sodium nitrate makes adequate use of the results of the theory of space-groups. It is quite certain nevertheless that the correct atomic arrangement has been



TABLE IV.  
*The Crystal Structures of Simple and Complex Halides, Cyanides, Etc.*

Compound.	System of Symmetry.	Type of Arrangement.	Text Figure of Unit Cell.	Dimensions of Unit Cell.	Class of Determination.
LiH.....	Cubic	NaCl	Fig. 6	$a = 4.10$	IIA
LiF.....	Cubic	NaCl	Fig. 6	$a = 4.14, 4.02$	IIA
LiCl.....	Cubic	NaCl	Fig. 6	$a = 5.17$	IA
LiBr.....	Cubic	NaCl	Fig. 6	$a = 5.48$	IA
LiI.....	Cubic	NaCl	Fig. 6	$a = 6.06$	IA
NaF.....	Cubic	NaCl	Fig. 6	$a = 4.61, 4.68$	IA
NaCl.....	Cubic	NaCl	Fig. 6	$a = 5.628$	IIA
NaBr.....	Cubic	NaCl	Fig. 6	$a = 5.95, 6.02$	IA
NaI.....	Cubic	NaCl	Fig. 6	$a = 6.47, 6.50$	IA
KF.....	Cubic	NaCl	Fig. 6	$a = 5.36, 5.38$	IA
KCl.....	Cubic	NaCl	Fig. 6	$a = 6.26$	IIA
KBr.....	Cubic	NaCl	Fig. 6	$a = 6.59, 6.60$	IA
KI.....	Cubic	NaCl	Fig. 6	$a = 7.11, 7.10$	IA
RbF.....	.....	.....	.....	.....	.....
RbCl.....	Cubic	NaCl	Fig. 6	$a = 6.60$	IA
RbBr.....	Cubic	NaCl	Fig. 6	$a = 6.93$	IA
RbI.....	Cubic	NaCl	Fig. 6	$a = 7.36, 7.31$	IA
CsF.....	Cubic	NaCl	Fig. 6	$a = 6.03$	IA
CsCl.....	Cubic	CsCl	Fig. II	$a = 4.12$	IIA
CsBr.....	Cubic	CsCl	Fig. II	$a = 4.30$	IA
CsI.....	Cubic	CsCl	Fig. II	$a = 4.55$	IA
TlCl.....	Cubic	CsCl	Fig. II	$a = 3.85$	IIA
CuCl.....	Cubic	ZnS	Fig. 9	$a = 5.49, 5.36$	IA
CuBr.....	Cubic	ZnS	Fig. 9	$a = 5.82, 5.75$	IA
CuI.....	Cubic	ZnS	Fig. 9	$a = 6.10, 6.07$	IA
AgCl.....	Cubic	NaCl	Fig. 6	$a = 5.56, 5.52$	IIA
AgBr.....	Cubic	NaCl	Fig. 6	$a = 5.78$	IIA
AgI (low).....	Hexagonal	ZnO	Fig. 7	$a = 4.59; c = 7.53$	IA



AgI (high).....	Cubic	Great complexity	.....	.....	.....	.....
NH <sub>4</sub> Cl (low).....	Cubic	NH <sub>4</sub> Cl	Fig. 12	$a = 3.859$	.....	.....
NH <sub>4</sub> Cl (high).....	Cubic	NaCl type	.....	$a = 6.533$ at $250^{\circ}$	.....	IA
NH <sub>4</sub> Br (low).....	Cubic	NH <sub>4</sub> Cl	Fig. 12	$a = 3.988$	.....	Incomplete
NH <sub>4</sub> Br (high).....	Cubic	NaCl type	.....	$a = 6.90$ at $250^{\circ}$	.....	IIA
NH <sub>4</sub> I.....	Cubic	NaCl type	.....	.....	.....	Incomplete
PH <sub>4</sub> I.....	Tetragonal	PH <sub>4</sub> I	Fig. 13	$a = 6.34$ ; $c = 4.62$	.....	I?
N(CH <sub>3</sub> )I.....	Tetragonal	.....	.....	.....	.....	IB
KCN.....	Cubic	NaCl type	.....	$a = 6.54$ , $6.55$	.....	IA
CaF <sub>2</sub> .....	Cubic	CaF <sub>2</sub>	Fig. 14	$a = 5.452$ , $5.478$ , $5.455$ , $5.49$	.....	IIA
BaF <sub>2</sub> .....	Cubic	CaF <sub>2</sub>	Fig. 14	$a = 6.20$	.....	IIA
CdI <sub>2</sub> .....	Hexagonal	Mn(OH) <sub>2</sub>	Fig. 8	$a = 4.24$ ; $c = 6.84$	.....	I?
N <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....	Cubic	Pyrite type	Fig. 15	$a = 7.89$	.....	IA
NiCl <sub>2</sub> .6NH <sub>3</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 10.09$	.....	IA
NiBr <sub>2</sub> .6NH <sub>3</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 10.48$	.....	IA
NiI <sub>2</sub> .6NH <sub>3</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 11.01$	.....	IA
CsCl <sub>2</sub> I.....	Hexagonal	CsCl <sub>2</sub> I	Fig. 17	$a = 5.46$ ; $a = 70^{\circ} 42'$	.....	IB
KI <sub>3</sub> .....	Monoclinic	.....	.....	.....	.....	IIIB
K <sub>2</sub> Zn(CN) <sub>4</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	$a = 12.54$	.....	IA
K <sub>2</sub> Cd(CN) <sub>4</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	$a = 12.84$	.....	IA
K <sub>2</sub> Hg(CN) <sub>4</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	$a = 12.76$	.....	IA
K <sub>2</sub> PtCl <sub>4</sub> .....	Tetragonal	K <sub>2</sub> PtCl <sub>4</sub>	Fig. 19	$a = 6.99$ ; $c = 4.13$	.....	I?
K <sub>2</sub> PdCl <sub>4</sub> .....	Tetragonal	K <sub>2</sub> PtCl <sub>4</sub>	Fig. 19	$a = 7.01$ ; $c = 4.10$	.....	I?
(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub> .....	Tetragonal	K <sub>2</sub> PtCl <sub>4</sub>	Fig. 19	$a = 7.21$ ; $c = 4.26$	.....	I?
(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 9.843$	.....	IA
K <sub>2</sub> SnCl <sub>6</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 9.99$	.....	IA
(NH <sub>4</sub> ) <sub>2</sub> SnCl <sub>6</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 10.05$	.....	IA
(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> .....	Cubic	NiCl <sub>2</sub> .6NH <sub>3</sub>	Fig. 16	$a = 8.38$	.....	IA



given not only because of the excellent accord with the experimental data, but also on account of the agreement with the more completely studied members of the calcite group. A single spectrometric observation<sup>86</sup> upon a cleavage face has been said to agree with a structure identical with that previously assigned to calcite. A study<sup>126</sup> of spectrum and Laue photographs gave results in substantial agreement.

The unit cell is a rhombohedron containing two chemical molecules in the following coördinate positions:

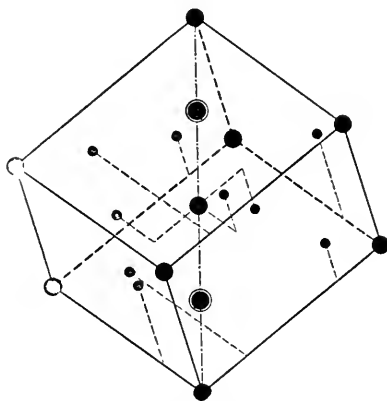
Oxygen:  $000$ ;  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

Sodium:  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ;  $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ .

Nitrogen:  $u\bar{u}0$ ;  $\bar{u}0u$ ;  $0u\bar{u}$ ;  $\frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2}$ ;  $u+\frac{1}{2},\frac{1}{2},\frac{1}{2}-u$ ;  $\frac{1}{2},\frac{1}{2}-u,u+\frac{1}{2}$ .

The spectrometric measurement is held to agree with a value of

FIG. 20.



The unit rhombohedron of the "calcite arrangement." No attempt has been made to indicate the correct shape of this unit. The carbon atoms (of calcite) are shown by large, the oxygen atoms by small black circles.

$u$  that is close to  $\frac{1}{4}$ . The study of Laue photographs also shows that  $u$  must lie very near indeed to 0.25. The length of the side of this unit rhombohedron (Fig. 20), the angle between the axes of which is  $48^{\circ}6'$ , is found to be 6.320A.U. A somewhat better idea of the marshalling of the atoms within the crystal is furnished by the representation of the larger construction cell of atoms which accompanies the spectrometric studies.

SODIUM CHLORATE AND SODIUM BROMATE.—In one of the two investigations carried out upon these cubic crystals powder photographic data<sup>127</sup> were used, in the other spectrometric measurements.<sup>128</sup> Both agree in deducing the same atomic arrangement but they differ in the positions assigned to the oxygen atoms. This is not surprising, however, when it is realized that the five



variable parameters that exist can only be established by a procedure of trial. The coördinates of the positions of the atoms within the unit cube which contains four chemical molecules must be as follows:

Sodium:  $uuu, u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}; \bar{u}, u + \frac{1}{2}, \frac{1}{2} - u; \frac{1}{2} - u, \bar{u}, u + \frac{1}{2}.$

Halogen: a similar set of positions in  $v$ .

Oxygen: the twelve generally equivalent positions of the space-group  $T^4$ :  
 $xyz; x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}; \bar{x}, y + \frac{1}{2}, \frac{1}{2} - z; \frac{1}{2} - \bar{x}, y, z + \frac{1}{2};$   
 $zxy; \bar{z}, x + \frac{1}{2}, \frac{1}{2} - y; \frac{1}{2} - z, \bar{x}, y + \frac{1}{2}; z + \frac{1}{2}, \frac{1}{2} - x, \bar{y};$   
 $yzx; \frac{1}{2} - y, \bar{z}, x + \frac{1}{2}; y + \frac{1}{2}, \frac{1}{2} - z, \bar{x}; \bar{y}, z + \frac{1}{2}, \frac{1}{2} - x.$

*Sodium Chlorate*,  $\text{NaClO}_3$ .—The length of the side of the unit cube has been taken as:  $a = 6.55 \text{ A.U.}^{127}$  and  $a = 6.56 \text{ A.U.}^{128}$ . The latter of these two values is calculated from the density  $\rho = 2.49$ . In the two investigations the values of the parameters defining the positions of the atoms have been chosen as:  $u = 0.083$  or  $0.08$ ,  $v = 0.417$  or  $0.43$ ,  $x = 0.50$  or  $0.30$ ,  $y = 0.417$  or  $0.59$ ,  $z = 0.306$  or  $0.47$ . It will be observed that there is close agreement in the positions of the sodium and chlorine atoms, but that the oxygen atoms are differently placed.

*Sodium Bromide*,  $\text{NaBrO}_3$ .—The length of the side of the unit cube is given as:  $a = 6.74 \text{ A.U.}^{127}$  and  $a = 6.71 \text{ A.U.}^{128}$ . The latter is calculated from a density  $\rho = 3.30$ . In one of the investigations <sup>127</sup> the same coördinate positions are considered to apply to both the bromate and the chlorate; for the other  $u = 0.09$ ,  $v = 0.41$ ,  $x = 0.30$ ,  $y = 0.60$  and  $z = 0.47$ .

There can be little doubt of the general correctness of this structure and it is also likely that the sodium and halogen atoms have been placed near to their true positions. Of the two assignments of position to the oxygen atoms, those based upon spectrometric measurements are in somewhat better agreement with the experimental data, though it must be remembered that their precise values will be influenced by the scattering assumptions used. It is interesting to note that for those reflections which give separate lines in the powder photographs both sets of atomic positions are in about equally good agreement with the experimental data: The less satisfactory character of the first assignment appears in those planes which can only be separately studied with spectrometric or Laue photographic methods.



THE NITRATES OF BARIUM, STRONTIUM, LEAD AND CALCIUM.—From an investigation<sup>129</sup> which has not been published in detail, it is said that spectrographic measurements upon the first three of these crystals show four chemical molecules to be associated with the unit cube. From this fact and Laue photographic data they are assigned to the space-group  $T_h^6$  (the same as that of pyrite); hence the atoms have the following coördinate positions:

Divalent metal atoms:	000; $\frac{1}{2}\frac{1}{2}0$ ; $0\frac{1}{2}\frac{1}{2}$ ; $\frac{1}{2}0\frac{1}{2}$ .
Nitrogen atoms:	$uuu$ ; $u + \frac{1}{2}, \frac{1}{2} - u, \bar{u}$ ; $\bar{u}, u + \frac{1}{2}, \frac{1}{2} - u$ ; $\frac{1}{2} - u, \bar{u}, u + \frac{1}{2}$ ; $\bar{u}\bar{u}\bar{u}$ ; $\frac{1}{2} - u, u + \frac{1}{2}, u$ ; $u, \frac{1}{2} - u, u + \frac{1}{2}$ ; $u + \frac{1}{2}, u, \frac{1}{2} - u$ .
Oxygen atoms:	the twenty-four generally equivalent positions of the <sup>152</sup> space-group $T_h^6$ .

The values of these four parameters were not determined and it would scarcely seem feasible to try to do so at the present time, but it is said that  $u = \frac{1}{4}$ , and  $x = \frac{1}{4}$ ,  $y = \frac{1}{4}$ ,  $z = 0$ , may be chosen as approximate positions. The marked hemihedral character of the Laue photographs must preclude the possibility of these coördinate values being exactly fulfilled. No determination of dimensions accompany this paper. In spite of the fragmentary character of the reported results, it is probably correct in its general assignment of structure. Recently powder photographic data<sup>130</sup> have been collected from these crystals and from calcium nitrate. A structure is given of the same type as the one just described and an assignment of parameters for the nitrogen and oxygen atoms made. These crystals are even less favorable for such an estimation of variable parameters than was sodium chlorate, because all of the atoms whose positions are to be determined have relatively slight scattering powers. In view of the difficulties apparently encountered by powder photographic data in placing the oxygen atoms in sodium chlorate, the nitrogen and oxygen positions assigned to these crystals must be of uncertain value. The lengths of the sides of the unit cubes for these crystals are determined to be:

Crystal.	$a \times 10^{-8}$ cm.
$\text{Ca}(\text{NO}_3)_2$	7.60
$\text{Sr}(\text{NO}_3)_2$	7.81
$\text{Ba}(\text{NO}_3)_2$	8.11
$\text{Pb}(\text{NO}_3)_2$	7.84



HYDRATES AND AMMONATES OF NITRATES, CHLORATES, ETC.—Two of these crystals have been studied: Zinc bromate hexahydrate and nickel nitrate hexammonate. Both have been investigated with spectrographic and Laue photographic data. The arrangement of their atoms can be determined with entire definiteness though it is not now practicable to try to locate some of these atoms with precision. The coördinates defining the atomic positions are the same for both (except for the different numbers of hydrogen atoms in the two compounds) and the same, as far as they go, as the coördinates of the atoms of barium, strontium and lead nitrates which have just been considered. Consequently the coördinates will not be repeated. The oxygen atoms of the water groups and the nitrogen atoms of the ammonia groups will also occupy the generally equivalent positions of  $T_h^6$  with values of  $x$ ,  $y$  and  $z$  which are different from those of the oxygen atoms of the anion groups. The hydrogen atoms must likewise occupy two or three sets, as the case may be, of generally equivalent positions with still different coördinate values.

*Zinc Bromate Hexahydrate*,<sup>131</sup>  $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ .—The length of the side of the unit cube containing four chemical molecules was stated to be:  $a = 10.31 \text{ A.U.}$  No estimation is offered of the variable parameters within this structure.

*Nickel Nitrate Hexammonate*,<sup>132</sup>  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ .—The length of the side of the unit cube was found to be:  $a = 10.96 \text{ A.U.}$  From the general character of the Laue photographic data it is probable that the coördinates for the ammonia nitrate atoms are close to  $v00$ , where  $v$  is about  $\frac{1}{4}$ . Other than this no estimate of the variable parameters within the structure can be offered. This compound is the same as the one which has previously been described as  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ .

#### CARBONATES.

Measurements have been recorded upon the related minerals: Calcite, dolomite, rhodochrosite and siderite. Calcite, the best studied, has been subjected to a detailed treatment by various investigators.<sup>86, 133, 134, 135</sup> They all agree in giving to it, and to the other members of the group, the same atomic arrangement which has been discussed for sodium nitrate with carbon atoms replacing the nitrogen (Fig. 20).

*Calcite*,  $\text{CaCO}_3$ .—The original determination<sup>86</sup> of structure was made with spectrometric measurements. This has since been



established with apparent certainty and positions for the oxygen atoms deduced with Laue photographic data.<sup>134, 135</sup> There is, however, a sharp difference of opinion concerning the value of the parameter  $u$  for oxygen. The original spectrometric measurements<sup>86</sup> and one of the studies based upon Laue photographs<sup>134</sup> agree with one another in making  $u$  about 0.30. The later, and more accurate, spectrometric observations,<sup>133</sup> and the other work based upon Laue photographs,<sup>135</sup> find that  $u$  must lie close to 0.25.

This discrepancy calls for some discussion. In the first place, the spectrometric results, whatever may be their value for this purpose, are definitely in favor of the lower parameter. In one of the determinations<sup>134</sup> of the positions of the oxygen atoms, based upon Laue photographic data, a more or less quantitative use seems to have been made of the so-called laws of scattering. In view of the probably only qualitative correctness of these laws it would seem that this procedure does not necessarily form a faithful guide for placing atoms. In the other determination,<sup>135</sup> an attempt was made to avoid the use of these "laws" where possible and in no case to make anything but a roughly qualitative use of them. Thus only planes to which no atoms but oxygen contributed were used for locating these atoms and the only intensity criteria that were called into play were observations of the existence of large differences of intensity between pairs of reflections. It was only after a prolonged study of Laue photographs that data were found to decide between the two positions of 0.25 and 0.30; eventually reflection data were met that appear in flat contradiction with the higher value of  $u$ . This latter determination<sup>133, 135</sup> of  $u = 0.25$ , in its avoidance of a quantitative use of scattering assumptions known to hold only qualitatively, thus is the safer one.

The spacing between cleavage planes is generally taken as the X-ray standard of wave-length. The length of the correct unit rhombohedron containing two chemical molecules (Fig. 20) is 6.360A.U.; the angle between the axes  $46^{\circ}6'$ . In one of the papers on calcite and the other members of this group,<sup>135</sup> the dimensions of the unit cell were incorrectly stated. As in the case of sodium nitrate, a better idea of the atomic arrangement can be obtained from viewing a larger construction rhombohedron.<sup>86</sup> This is the crystallographically chosen unit, the equal angles between rhombohedral axes being  $101^{\circ}55'$ .



*Rhodochrosite*,  $\text{MnCO}_3$ .—Spectrometer,<sup>86</sup> spectrographic and Laue photographic data<sup>135</sup> have been studied. The structure is the same as that of calcite except that a different value is to be assigned to the oxygen parameter. The Laue photographs have been used, as in one of the treatments<sup>135</sup> of calcite, to place the oxygen atoms with only a qualitative use of one of the "laws" of scattering. The value thus chosen\* is around 0.27. The length of the side of the unit rhombohedron containing two chemical molecules is 5.836A.U.; the angle between the axes  $47^\circ 45'$ .

*Siderite*,  $\text{FeCO}_3$ .<sup>86, 135</sup>—The Laue photographic data,<sup>135</sup> though not so good as those for the two previous salts, showed no difference between the parameter for this crystal and for rhodochrosite. It may consequently be taken as probably close to 0.27. The length of the side of the unit rhombohedron (Fig. 20) also approaches that for rhodochrosite:  $a = 5.822\text{A.U.}$  The angle between the axes is  $47^\circ 45'$ .

*Dolomite*,  $\text{CaMg}(\text{CO}_3)_2$ .—The single reflection spectrum<sup>86</sup> that has been taken is said to agree with a structure similar to that of the other calcite group minerals.

#### SILICATES.

Attempts have been made to study the atomic arrangement in two silicates, olivine and garnet. Both have made some use of the results of the theory of space-groups, though in their present forms neither is entirely satisfactory.

*Olivine*,<sup>136</sup>  $(\text{Mg,Fe})_2\text{SiO}_4$ .—The ratio of magnesium to iron in the specimen studied was about six to one. Many Laue photographs in different orientations were prepared from this orthorhombic crystal and the planes corresponding to the observed spots identified. Use of these data does not seem to have been made in the subsequent attempt to establish the space-group of olivine. Reflection spectra give a unit cell with dimensions corresponding to the accepted axial ratio. They are also thought to show that the corresponding space-group is probably  $V_h$ <sup>16</sup>. In view of the apparent failure to establish this cell as the simplest one, and not merely one of a number of crystallographically possible units, there is some doubt concerning the uniqueness of this determination.

---

\* The early estimation<sup>86</sup> of  $u$ , based upon approximate spectrometric measurements, placed the oxygen parameter for the other crystals than calcite considerably above 0.30.



*Garnet.*<sup>137</sup>—Crystals of garnet have the general composition  $R_3''R_2'''(SiO_4)_3$ , where  $R''$  and  $R'''$  can be various di- and trivalent metallic elements. The one measured was a ferrous aluminum garnet in which about one-third of the iron was replaced by manganese. Both spectrographic and Laue photographic observations were made upon this crystal though data have never been published. There appears to be some conflict between the structure and the determination of the number of molecules within the unit cell. A study in the light of recent procedure probably is required before the results of this investigation can be taken as firmly established.

#### SULFATES, MOLYBDATES, TUNGSTATES, ETC.

*Alkali Sulfates.*<sup>138</sup>—Spectrometric observations have been made upon crystals of the isomorphous series of the sulfates of potassium, ammonium, rubidium and caesium, primarily for the purpose of testing the hypothesis of valency-volume. These measurements will form a valuable source of data in the future, but at present they are quite incapable by themselves of establishing the arrangement of the atoms in these crystals.

*Silver Molybdate,  $Ag_2MoO_4$ .*—The structure<sup>139</sup> of crystals of silver molybdate has been established from spectrographic and Laue photographic data. The coördinate positions of the atoms within the unit cube (Fig. 18) are the same as those of the corresponding atoms of  $K_2Zn(CN)_4$ : Silver and potassium atoms, molybdenum and zinc atoms, and oxygen and either the carbon or nitrogen atoms having the same coördinates. The parameter for oxygen could not be accurately determined, probably because of the much greater scattering powers of the other atoms, but it is shown that  $u$  must have a value that is close to 0.37 and can scarcely be greater than 0.40 or less than 0.34. The length of the side of this unit cube which contains eight molecules is found to be:  $a = 9.26A.U.$

*Scheelite,  $CaWO_4$ .*—Spectrometric measurements<sup>140</sup> from various faces have been made upon crystals of scheelite. Such observations are not sufficient to determine the structure of this tetragonal crystal with any degree of certainty.

*Wulfenite,  $PbMoO_4$ .*—The same treatment<sup>140</sup> has been given to this crystallographically related crystal.

*Alums.*—An early attempt<sup>141</sup> was made to obtain the structure of potash alum. Spectrometer data<sup>142</sup> have been published



for the aluminum and chromium potash alums and for aluminum and iron ammonium alums. On the basis of these results a structure was assigned which placed four sulfate sulfur atoms in a group separated from oxygen atoms. This was chemically so improbable that a more reasonable structure has been sought from these same data. This latter investigation<sup>143</sup> is held to show that the recorded experimental data require  $T_h^2$  as the corresponding space-group. An atomic arrangement is discussed which is a special case of this space-group and which besides accounting for the experiments has the added advantage of not doing violence to chemical conceptions. In other cases, of which rutile is typical, a spectrometer study as ordinarily carried out has so clearly shown its insufficiency as a means of recording correct diffraction data that more conclusive experiments are to be desired.

The lengths of the sides of the unit cubes containing four chemical molecules for the alums<sup>142</sup> measured are:

Crystal.	$a \times 10^{-8}$ cm.
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	12.08
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	12.00
$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	12.14
$\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	11.93

#### BORATES, ALUMINATES, FERRITES, ETC.

*Tourmaline.*<sup>144</sup>—Much Laue photographic and spectrographic data have been published upon crystals of tourmaline. From these, notably the latter, an attempt has been made to establish the corresponding space-group. No effort has been made to determine the atomic arrangement more intimately.

*Spinel Group*,  $\text{R}''\text{R}_2'''\text{O}_4$  where  $\text{R}''$  and  $\text{R}'''$  are various di- and trivalent metal elements. Some data have been published upon three members of this group: Magnetite ( $\text{Fe}_3\text{O}_4$ ), spinel ( $\text{MgAl}_2\text{O}_4$ ) and gahnite ( $\text{ZnAl}_2\text{O}_4$ ). Spectrometric measurements,<sup>145</sup> in the last case only upon a single face, have been recorded for all three. Laue photographs<sup>146</sup> have been taken of the first two. Powder photographs<sup>70</sup> of magnetite, which were not used for structure determination, and of  $\text{Co}_3\text{O}_4$ , which is said to give spectra similar to  $\text{Fe}_3\text{O}_4$  and is probably isomorphous with it, are also available. Neither of the determinations of crystal structure, the one based upon spectrometric observations alone,<sup>145</sup> the other developed from a detailed consideration of Laue photographs, has been carried out in a conclusive fashion.



The structure deduced by both is, however, the same. Especially because of the excellent character of the second investigation which used space-group results for the purposes of description but apparently not as a direct means of analysis, and because of the agreement of these structures with the more completely studied potassium zinc cyanide and silver molybdate, the correct atomic arrangement for these spinels has undoubtedly been selected. Since this structure is the same as that of the previously discussed potassium zinc cyanide, its atomic arrangement will be described in terms of that crystal. The coördinate positions of the trivalent metal of the spinel are the same as those of potassium, the divalent atoms have the same positions in the two cases and the oxygen atoms have the same set of positions that is occupied by either the carbon or the nitrogen atoms (Fig. 18). With the use of Laue photographic data the value of the parameter  $u$  for oxygen could be most accurately determined in the magnesium aluminum spinel as very close to  $3/8$ , the best fit for scattering assumptions used being 0.384. In magnetite the oxygen atoms also lie very close to  $3/8$ , but because of the greater scattering power of the iron atoms an appreciable variation from precisely this position could not well be detected. From the spectrometric measurements the length of the side of the unit cube of magnetite which contains eight chemical molecules has been determined as:  $a = 8.30\text{A.U.}$  Dimensions have not been stated for the other two crystals (though, of course, values can be calculated from the density).

*Chalcopyrite*,  $\text{CuFeS}_2$ .—Spectrometric measurements<sup>147</sup> of this tetragonal crystal have been made and a structure suggested to account for them. They are so inadequate for the establishing of its correct atomic arrangement, however, that until further work has been carried out this structure cannot be considered as known.

#### PHOSPHATES, ETC.

*Xenotime*,<sup>80, 112</sup>  $\text{YPO}_4$ .—This is the only member of the group which has been subjected to any X-ray examination. The study of this crystal was carried out at the same time and in the same manner as those of rutile and the other tetragonal minerals which it somewhat resembles; hence it is subject to the same insufficiencies as they.



## ORGANIC COMPOUNDS.

The crystal structure of no organic compound has been adequately and completely determined. Only one<sup>148</sup> of the few that have been measured, sodium acid acetate, is cubic and has been subjected to the detailed treatment that the use of the results of the theory of space-groups makes possible. Besides this relatively simple substance, the crystal structure of which nevertheless was too complicated for complete elucidation, some powder photographic<sup>78</sup> and spectrometric<sup>149</sup> observations have been made upon numerous organic substances. As determinations of crystal structure the treatment of these latter data are valueless. A determination of the shape and dimensions of the molecule of liquid benzene<sup>150</sup> has been published; but is not in any sense unique.

*Sodium Acid Acetate*,  $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$ .—With the aid of spectrographic and Laue photographic data, it is shown<sup>148</sup> that the unit cube of this crystal must contain twenty-four chemical molecules, and that the corresponding space-group is probably  $T_h$ <sup>7</sup>. This number of atoms within the unit is so great that even with the knowledge of the appropriate space-group no definite picture of the manner of arrangement of these atoms can be obtained. The length of the side of this large unit is given as 15.98A.U.

The exceedingly complicated character of this crystal may serve as a warning of the difficulties that will be encountered when organic compounds are studied. It clearly shows, if any indications aside from the general insufficiency of the methods used were required, of how little use as determinations of correct atomic arrangement are the other studies<sup>78, 149</sup> to which reference has just been made. For this reason they can receive no detailed treatment at this point.

**SUMMARY OF THE CRYSTAL STRUCTURES OF  
NITRATES, CARBONATES, ETC.**

The results of crystal structure determinations of the nitrates and crystals following them in the classification of Table I are summarized in Table V.



TABLE V.  
*The Crystal Structures of the Nitrates, Carbonates, Etc.*

Compound.	System of Symmetry.	Type of Arrangement.	Text Figure of Unit Cell.	Dimensions of Unit Cell.	Class of Determination.
NaNO <sub>3</sub> .....	Hexagonal	Calcite	Fig. 20	$a = 6.32; a = 48^{\circ} 6'$	IB
NaClO <sub>3</sub> .....	Cubic	NaClO <sub>3</sub>	.....	$a = 6.56, 6.55$	IA
NaBrO <sub>3</sub> .....	Cubic	NaClO <sub>3</sub>	.....	$a = 6.74, 6.71$	IA
Ca(NO <sub>3</sub> ) <sub>2</sub> .....	Cubic	Pyrite type	.....	$a = 7.60$	IIA
Sr(NO <sub>3</sub> ) <sub>2</sub> .....	Cubic	Pyrite type	.....	$a = 7.81$	IB
Ba(NO <sub>3</sub> ) <sub>2</sub> .....	Cubic	Pyrite type	.....	$a = 8.11$	IB
Pb(NO <sub>3</sub> ) <sub>2</sub> .....	Cubic	Pyrite type	.....	$a = 7.84$	IB
Zn(BrO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O.....	Cubic	Zn(BrO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	.....	$a = 10.31$	IA
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6NH <sub>3</sub> .....	Cubic	Zn(BrO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	.....	$a = 10.96$	IA
CaCO <sub>3</sub> .....	Hexagonal	Calcite	Fig. 20	$a = 6.36; a = 46^{\circ} 6'$	IA
MnCO <sub>3</sub> .....	Hexagonal	Calcite	Fig. 20	$a = 5.84; a = 47^{\circ} 45'$	IA
FeCO <sub>3</sub> .....	Hexagonal	Calcite	Fig. 20	$a = 5.82; a = 47^{\circ} 45'$	IA
Olivine.....	Orthorhombic	.....	.....	.....	Incomplete
Garnet.....	Cubic	.....	.....	.....	Uncertain
Alkali sulfates.....	Orthorhombic	.....	.....	.....	IIIB
Ag <sub>2</sub> MoO <sub>4</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	$a = 9.26$	IA
CaWO <sub>4</sub> .....	Tetragonal	.....	.....	.....	IIIB
PbMoO <sub>4</sub> .....	Tetragonal	.....	.....	.....	IIIB
KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O.....	Cubic	.....	.....	$a = 12.08$	III
KCr(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O.....	Cubic	.....	.....	$a = 11.93$	III
NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O.....	Cubic	.....	.....	$a = 12.00$	III
NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O.....	Cubic	.....	.....	$a = 12.14$	III
Fe <sub>3</sub> O <sub>4</sub> .....	Cubic	.....	.....	$a = 8.30$	IB
MgAl <sub>2</sub> O <sub>4</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	.....	IB
CuFeS <sub>2</sub> .....	Cubic	K <sub>2</sub> Zn(CN) <sub>4</sub>	Fig. 18	.....	IIIB
YPO <sub>4</sub> .....	Tetragonal	.....	.....	.....	IIIB
NaH(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .....	Cubic	.....	.....	$a = 15.98$	IA (Inc.)



## CONCLUSIONS.

The known failures to assign correct crystal structures supply confirmation of the point of view expressed in the introduction to this paper. The following are some well-established examples:

*Graphite*.—Powder data have given two different structures to this crystalline arrangement.

*Antimony and Bismuth*.—Four atomic arrangements have been given to these similar metals through data drawn from spectrometric and powder data.

*Carborundum*.—Spectrometric observations have been used to assign a distorted "zinc sulfide arrangement" to the atoms of CSi; later these same data were considered to yield this arrangement undistorted. Powder data have been thought to show a structure which is a mixture of hexagonal and cubic arrangements within the same crystal. Recent crystallographic and Laue photographic measurements, however, appear to show that three different forms of CSi crystals can exist together and that the structure of at least one of them is very complicated. From such data as are available it appears that the crystals studied with the spectrometer are the same as those investigated with Laue photographs; the results of the two investigations, nevertheless, are different. It is not apparent which or how many of the forms were subjected to powder measurement. The insufficiency of these individual methods taken alone is evident.

*Ice*.—Three different structures have come out of two experimental studies upon ice, one spectrographic and the other powder photographic. A theoretically well-worked treatment of Laue photographs has led to still a different arrangement. Because of the uncertainty concerning the individual character of the specimens used in the last-mentioned investigation, it cannot now be considered as any more certain than the others. Even the dimensions of unit cells assigned by these different studies are not related to one another.

*Beryllium Oxide*.—By ascribing certain of the lines appearing in powder photographs to impurities in the sample, a cubic structure has been given to this hexagonal crystal.

*Zinc Oxide*.—Spectrometric observations were believed to have established a structure for this crystal. A subsequent application of space-group considerations, however, brought to light



another simple atomic arrangement which was in equally good agreement with the existing data and in almost as good agreement with any data that can now be obtained.

*Silica*.—Two different structures have been assigned to quartz upon the basis of spectrometer measurements.

*Rutile*.—The spectrometric data as ordinarily collected, and consequently the structures that have been assigned to this crystal by the two investigations that have been made, are different.

*Silver Iodide*.—Two separate determinations with powder data have given this hexagonal crystal a cubic structure. A careful study with both Laue photographic and powder data has since shown that the principal powder lines are in close agreement with positions for a structure with cubic symmetry. Silver iodide is a clear case against crystal structure determinations based upon unaided powder photographic data.

*Tetramethylammonium Iodide*.—On the basis of spectrometer measurements a structure was assigned to this crystal which did not group the four methyl carbon atoms about the corresponding nitrogen atom. This appeared so improbable that upon search another structure was found which was chemically more probable and in equally good agreement with the experimental data.

*Sodium Chlorate*.—Two determinations of the structure of sodium chlorate, one with powder data the other from spectrometric measurements, give the same kind of arrangement but with different positions for the oxygen atoms. The powder data, however, are in equally good agreement with both sets of oxygen positions; the spectrometric results disagree with the arrangement based simply upon powder data only for those planes which cannot be separated in powder experiments.

*Potash Alum*.—On the basis of spectrometer data alone an atomic arrangement was assigned to this crystal which grouped four sulfur atoms together. This structure was in such disagreement with chemical notions that another grouping of atoms was found which was in equally good agreement with the experimental data.

*Potassium Triiodide*.—On the basis of measurements made by a modified spectrometer technic, this monoclinic crystal has received a cubic structure.

In the face of these illustrations no further argument is required to show the practical necessity of adopting methods of



crystal structure study that make use of space-group results and of using to its full the crystallographic information concerning symmetry. These failures are amongst the relatively complicated crystals which either have a symmetry lower than cubic or are of considerable chemical complexity. This need becomes even more strikingly apparent when it is noted that few of these complicated crystals have been studied and when it is realized that the restricted field of simple cubic crystals has been quite thoroughly explored. The failure of the data that can be obtained by some of the methods of producing X-ray effects used alone must be convincing argument for taking a wider view towards diffraction experiments. Such an attitude, seeing in no one method an answer to all questions that may arise, rather employs in any particular case that procedure which is calculated to yield the most usable data.

## BIBLIOGRAPHY.

- <sup>1</sup> DANA: "System of Mineralogy."
- <sup>2</sup> P. GROTH: "Chemische Krystallographie," Leipzig, 1906.
- <sup>3</sup> A. W. HULL: *Phys. Rev.*, **10**, 661 (1917).
- <sup>4</sup> J. M. BIJVOET and A. KARSEN: *Proc. Roy. Acad. Sci. Amsterdam*, **23**, No. 9 (1922).
- <sup>5</sup> L. W. MCKEEHAN: *Proc. Nat. Acad. Sci.*, **8**, 254 (1922).
- <sup>6</sup> W. L. BRAGG: *Phil. Mag.*, **28**, 355 (1914).
- <sup>7</sup> L. VEGARD: *Phil. Mag.*, **31**, 83 (1916).
- <sup>8</sup> H. KAHLER: *Phys. Rev.*, **18**, 210 (1921).
- <sup>9</sup> L. VEGARD: *Phil. Mag.*, **32**, 65 (1916).
- <sup>10</sup> L. W. MCKEEHAN: *Proc. Nat. Acad. Sci.*, **8**, 270 (1922).
- <sup>11</sup> A. W. HULL: *Proc. Nat. Acad. Sci.*, **3**, 470 (1917).
- <sup>12</sup> H. BOHLIN: *Ann. d. Physik*, **61**, 421 (1920).
- <sup>13</sup> A. W. HULL: *Phys. Rev.*, **17**, 42 (1921).
- <sup>14</sup> P. NIGGLI: "Geometrische Krystallographie des Discontinuums," Leipzig, 1919.
- <sup>15</sup> L. W. MCKEEHAN and P. P. CIOFFI: *Phys. Rev.*, **19**, 444 (1922).
- <sup>16</sup> N. ALSEN and G. AMINOFF: *Geol. För. Förh.*, **44**, 124 (1922).
- <sup>17</sup> A. W. HULL: *Phys. Rev.*, **9**, 564 (1917).
- <sup>18</sup> P. SCHERRER: *Physikal. Z.*, **19**, 23 (1918).
- <sup>19</sup> A. W. HULL: *Phys. Rev.*, **17**, 571 (1921).
- <sup>20</sup> W. H. and W. L. BRAGG: *Nature*, **91**, 557 (1913).
- <sup>21</sup> P. P. EWALD: *Ber. Bayer. Akad. Wiss.*, p. 325 (1914).
- <sup>22</sup> P. DEBYE and P. SCHERRER: *Physikal. Z.*, **17**, 277 (1916).
- <sup>23</sup> P. DEBYE and P. SCHERRER: *Physikal. Z.*, **18**, 291 (1917).
- <sup>24</sup> A. W. HULL: *Phys. Rev.*, **20**, 113 (1922).
- <sup>25</sup> W. GERLACH: *Physikal. Z.*, **23**, 114 (1922).



- <sup>20</sup> W. GERLACH: *Physikal. Z.*, **22**, 557 (1921).  
<sup>21</sup> A. W. HULL: *Science*, **52**, 227 (1920).  
<sup>22</sup> A. W. HULL: *Phys. Rev.*, **18**, 88 (1921).  
<sup>23</sup> N. H. KOLKMEIJER: *Verslag. Akad. Wetenschappen*, **31**, 155; *Proc. Roy. Acad. Sci. Amsterdam*, **25**, 125 (1922).  
<sup>24</sup> A. J. BIJL and N. H. KOLKMEIJER: *Chem. Weekblad*, **15**, 1264 (1918); *Proc. Roy. Acad. Sci. Amsterdam*, **21**, 405, 494, 501 (1919).  
<sup>25</sup> R. W. JAMES and N. TUNSTALL: *Phil. Mag.*, **40**, 233 (1920).  
<sup>26</sup> A. OGG: *Phil. Mag.*, **42**, 163 (1921).  
<sup>27</sup> R. W. JAMES: *Phil. Mag.*, **42**, 193 (1921).  
<sup>28</sup> W. H. and W. L. BRAGG: "X-rays and Crystal Structure," London, 1918, p. 227.  
<sup>29</sup> W. H. BRAGG: *Proc. Roy. Soc. A.*, **89**, 575 (1914).  
<sup>30</sup> P. STOLL: *Arch. Sci. Phys. Nat.*, **3**, 546 (1921).  
<sup>31</sup> P. DEBYE: *Physikal. Z.*, **18**, 483 (1917).  
<sup>32</sup> A. W. HULL: *Phys. Rev.*, **9**, 84 (1917).  
<sup>33</sup> A. W. HULL: *Phys. Rev.*, **14**, 540 (1919).  
<sup>34</sup> A. WESTGREN: *J. Iron and Steel Inst.*, No. 11 (1921).  
<sup>35</sup> A. WESTGREN and A. E. LINDH: *Zeitsch. physikal. Chem.*, **98**, 181 (1921).  
<sup>36</sup> L. W. MCKEEHAN: *Phys. Rev.*, **20**, 82 (1922).  
<sup>37</sup> M. R. ANDREWS: *Phys. Rev.*, **18**, 245 (1921).  
<sup>38</sup> A. WESTGREN and G. PHRAGMEN: *J. Iron and Steel Inst.*, 1922.  
<sup>39</sup> L. W. MCKEEHAN: *Phys. Rev.*, **19**, 537 (1922).  
<sup>40</sup> G. AMINOFF and G. PHRAGMEN: *Zeitsch. f. Krystal.*, **56**, 510 (1921).  
<sup>41</sup> H. BAUMHAUER: *Zeitsch. f. Krystal.*, **50**, 33 (1912); **55**, 249 (1915-20).  
<sup>42</sup> F. v. HAUER and P. KOLLER: *Zeitsch. f. Krystal.*, **50**, 260 (1915-20).  
<sup>43</sup> C. L. BURDICK and E. A. OWEN: *J. Am. Chem. Soc.*, **40**, 1749 (1918).  
<sup>44</sup> A. W. HULL: *Phys. Rev.*, **15**, 545 (1920).  
<sup>45</sup> H. ESPIG: *Abh. Sächs. Akad. Wiss. Leipzig*, (Math. Phys. Klasse) **38**, 53 (1921).  
<sup>46</sup> A. E. H. TUTTON: "Crystallography and Practical Crystal Measurement," Vol. i, p. 689, London, 1922.  
<sup>47</sup> A. W. HULL: *Phys. Rev.*, **13**, 292 (1919).  
<sup>48</sup> F. RINNE: *Ber. Verh. K. Sächs. Gesell. Wiss. Math. Nat.*, **69**, 57 (1917).  
<sup>49</sup> R. GROSS: *Centr. Min. Geol.*, 1919, p. 201.  
<sup>50</sup> A. ST. JOHN: *Proc. Nat. Acad. Sci.*, **4**, 193 (1918).  
<sup>51</sup> D. M. DENNISON: *Phys. Rev.*, **17**, 20 (1921); *Chem. News.*, **122**, 54 (1921).  
<sup>52</sup> W. H. BRAGG: *Proc. Phys. Soc. London*, **34**, 98 (1922).  
<sup>53</sup> W. H. and W. L. BRAGG: "X-rays and Crystal Structure," London, 1918, p. 155.  
<sup>54</sup> W. P. DAVEY: *Phys. Rev.*, **19**, 248 (1922).  
<sup>55</sup> P. NIGGLI: *Zeitsch. f. Krystal.*, **57**, 253 (1922).  
<sup>56</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **3**, 184 (1922).  
<sup>57</sup> W. GERLACH: *Zeitsch. f. Physik*, **9**, 184 (1922).  
<sup>58</sup> W. L. BRAGG: *Proc. Roy. Soc. A.*, **89**, 248 (1913).  
<sup>59</sup> A. W. HULL: *Proc. Am. Inst. Elec. Engin.*, **38**, 1171 (1919).  
<sup>60</sup> W. P. DAVEY and E. O. HOFFMAN: *Phys. Rev.*, **15**, 333 (1920).



- <sup>87</sup> W. GERLACH and O. PAULI: *Zeitsch. f. Physik*, **7**, 116 (1921).  
<sup>88</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **1**, 138 (1921).  
<sup>89</sup> E. SCHIEBOLD: *Zeitsch. f. Krystal.*, **56**, 430 (1921).  
<sup>90</sup> J. A. HEDVALL: *Arkiv. Kemi Mineral. Geol.*, **8**, No. 11; *Zeitsch. anorg. Chem.*, **120**, 327 (1922).  
<sup>91</sup> W. P. DAVEY: *Phys. Rev.*, **17**, 402 (1921).  
<sup>92</sup> W. L. BRAGG: *Phil. Mag.*, **39**, 647 (1920).  
<sup>93</sup> E. S. FEDEROV: *Bull. Acad. Sci. Petrograd*, p. 359 (1916).  
<sup>94</sup> G. AMINOFF: *Zeitsch. f. Krystal.*, **56**, 495 (1921).  
<sup>95</sup> G. AMINOFF: *Zeitsch. f. Krystal.*, **57**, 204 (1922).  
<sup>96</sup> P. SCHERRER: *Zeitsch. f. Krystal.*, **57**, 186 (1922).  
<sup>97</sup> J. BECKENKAMP: *Zeitsch. anorg. Chem.*, **110**, 290 (1920).  
<sup>98</sup> K. BECKER and W. JANCKE: *Zeitsch. physikal. Chem.*, **99**, 242 (1921).  
<sup>99</sup> C. M. WILLIAMS: *Proc. Roy. Soc.*, **93**, 418 (1917).  
<sup>100</sup> L. VEGARD: *Phil. Mag.*, **32**, 505 (1916).  
<sup>101</sup> W. H. and W. L. BRAGG: "X-rays and Crystal Structure," London, 1918, p. 169.  
<sup>102</sup> G. AMINOFF: *Geol. För. Förh.*, **41**, 407 (1919).  
<sup>103</sup> G. AMINOFF: *Zeitsch. f. Krystal.*, **56**, 506 (1921).  
<sup>104</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **2**, 239 (1921).  
<sup>105</sup> W. H. and W. L. BRAGG: *Proc. Roy. Soc. A.*, **89**, 276 (1914).  
<sup>106</sup> W. L. BRAGG: *Proc. Roy. Soc. A.*, **89**, 468 (1914).  
<sup>107</sup> R. W. G. WYCKOFF: "The Analytical Expression of the Results of the Theory of Space-groups," Carnegie Inst. Wash. Pub. 318 (1922).  
<sup>108</sup> M. K. SLATTERY: *Phys. Rev.*, **20**, 84 (1922).  
<sup>109</sup> W. H. and W. L. BRAGG: "X-rays and Crystal Structure," London, 1918, p. 173.  
<sup>110</sup> P. P. EWALD: *Physikal. Z.*, **15**, 399 (1914).  
<sup>111</sup> P. P. EWALD and W. FRIEDRICH: *Ann. d. Physik.*, **44**, 1183 (1914).  
<sup>112</sup> P. P. EWALD: *Ann. d. Physik*, **44**, 257 (1914).  
<sup>113</sup> M. MECHLING: *Abh. Sächs. Akad. Wiss. Leipzig*, **38**, 37 (1921).  
<sup>114</sup> J. M. BIJVOET and A. KARSEN: *Proc. Roy. Acad. Sci. Amsterdam*, **25**, Nos. 1 and 2 (1922).  
<sup>115</sup> R. W. G. WYCKOFF: *J. Wash. Acad. Sci.*, **11**, 429 (1921).  
<sup>116</sup> EUGEN POSNJAK and R. W. G. WYCKOFF: *J. Wash. Acad. Sci.*, **12**, 248 (1922).  
<sup>117</sup> W. P. DAVEY: *Phys. Rev.*, **18**, 102 (1921).  
<sup>118</sup> R. GLOCKER: *Ann. d. Physik*, **47**, 377 (1915); *Physikal. Z.*, **15**, 401 (1914).  
<sup>119</sup> W. H. BRAGG: *Proc. Roy. Soc. A.*, **89**, 246 (1913).  
<sup>120</sup> M. SIEGBAHN: *Phil. Mag.*, **37**, 601 (1919), etc.  
<sup>121</sup> R. G. DICKINSON, *J. Am. Chem. Soc.*, **44**, 2404 (1922).  
<sup>122</sup> W. P. DAVEY: *Phys. Rev.*, **19**, 538 (1922).  
<sup>123</sup> W. P. DAVEY and F. G. WICK: *Phys. Rev.*, **17**, 403 (1921).  
<sup>124</sup> R. W. G. WYCKOFF and EUGEN POSNJAK: *J. Am. Chem. Soc.*, **44**, 30 (1922).  
<sup>125</sup> G. AMINOFF: *Geol. För. Förh.*, **44**, 444 (1922).  
<sup>126</sup> G. AMINOFF: *Zeitsch. f. Krystal.*, **57**, 180 (1922).  
<sup>127</sup> R. B. WILSEY: *Phil. Mag.*, **42**, 262 (1921).



- <sup>108</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **4**, 469 (1922).  
<sup>109</sup> G. BARTLETT and I. LANGMUIR: *J. Am. Chem. Soc.*, **43**, 84 (1921).  
<sup>110</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **3**, 177 (1922).  
<sup>111</sup> P. NIGGLI: *Zeitsch. f. Krystal.*, **56**, 212 (1921-2).  
<sup>112</sup> L. VEGARD: *Phil. Mag.*, **33**, 395 (1917).  
<sup>113</sup> R. G. DICKINSON: *J. Am. Chem. Soc.*, **44**, 1489 (1922).  
<sup>114</sup> P. A. COOPER: *Nature*, **107**, 745 (1921).  
<sup>115</sup> R. M. BOZORTH: *J. Am. Chem. Soc.*, **44**, 317 (1922).  
<sup>116</sup> R. M. BOZORTH: *J. Am. Chem. Soc.*, **44**, 2232 (1922).  
<sup>117</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **5**, 15 (1923).  
<sup>118</sup> R. W. G. WYCKOFF: *J. Am. Chem. Soc.*, **44**, 1239 (1922).  
<sup>119</sup> P. SCHERRER and P. STOLL: *Zeitsch. anorg. Chem.*, **121**, 319 (1922).  
<sup>120</sup> R. W. G. WYCKOFF: *J. Am. Chem. Soc.*, **42**, 1100 (1920).  
<sup>121</sup> G. L. CLARK and W. DUANE: *Phys. Rev.*, **20**, 85 (1922).  
<sup>122</sup> R. G. DICKINSON: *J. Am. Chem. Soc.*, **44**, 774 (1922).  
<sup>123</sup> R. W. G. WYCKOFF and E. POSNJAK: *J. Am. Chem. Soc.*, **43**, 2292 (1921).  
<sup>124</sup> R. G. DICKINSON: *J. Am. Chem. Soc.*, **44**, 276 (1922).  
<sup>125</sup> R. M. BOZORTH: *J. Am. Chem. Soc.*, **44**, 1066 (1922).  
<sup>126</sup> R. W. G. WYCKOFF: *Phys. Rev.*, **16**, 149 (1920).  
<sup>127</sup> N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSSEN: *Proc. Roy. Acad. Sci. Amsterdam*, **23**, 644 (1921).  
<sup>128</sup> R. G. DICKINSON and E. A. GOODHUE: *J. Am. Chem. Soc.*, **43**, 2045 (1921).  
<sup>129</sup> S. NISHIKAWA and K. HUDINUKI: *Proc. Math. Phys. Soc. Tokyo*, **9**, 197 (1917).  
<sup>130</sup> L. VEGARD: *Zeitsch. f. Physik*, **9**, 395 (1922).  
<sup>131</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **4**, 188 (1922).  
<sup>132</sup> R. W. G. WYCKOFF: *J. Am. Chem. Soc.*, **44**, 1260 (1922).  
<sup>133</sup> W. H. BRAGG: *Phil. Trans. Roy. Soc.*, **215**, 253 (1915).  
<sup>134</sup> E. SCHIEBOLD: *Abh. Sächs. Akad. Wiss. Leipzig*, **36**, 65 (1919).  
<sup>135</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **50**, 317 (1920).  
<sup>136</sup> C. BERNDT: *Abh. Sächs. Akad. Wiss. Leipzig*, **38**, 1 (1921).  
<sup>137</sup> S. NISHIKAWA: *Proc. Math. Phys. Soc. Tokyo*, **9**, 194 (1917).  
<sup>138</sup> A. OGG and F. L. HOPWOOD: *Phil. Mag.*, **32**, 518 (1916).  
<sup>139</sup> R. W. G. WYCKOFF: *J. Am. Chem. Soc.*, **44**, 1994 (1922).  
<sup>140</sup> R. G. DICKINSON: *J. Am. Chem. Soc.*, **42**, 85 (1920).  
<sup>141</sup> T. TERADA: *Proc. Math. Phys. Soc. Tokyo*, **7**, 290 (1914).  
<sup>142</sup> L. VEGARD and H. SCHJELDERUP: *Ann. d. Physik*, **54**, 146 (1918).  
<sup>143</sup> P. NIGGLI: *Physikal. Z.*, **19**, 225 (1918).  
<sup>144</sup> C. KULASZEWSKI: *Abh. Sächs. Akad. Wiss. Leipzig*, **38**, 81 (1921).  
<sup>145</sup> W. H. BRAGG: *Phil. Mag.*, **30**, 305 (1915); *Nature*, **95**, 561 (1915).  
<sup>146</sup> S. NISHIKAWA: *Proc. Math. Phys. Soc. Tokyo*, **8**, 199 (1915).  
<sup>147</sup> C. L. BURDICK and J. H. ELLIS: *Proc. Nat. Acad. Sci.*, **3**, 644 (1917); *J. Am. Chem. Soc.*, **39**, 2518 (1917).  
<sup>148</sup> R. W. G. WYCKOFF: *Am. J. Sci.*, **4**, 193 (1922).  
<sup>149</sup> W. H. BRAGG: *Proc. Phys. Soc. London*, **34**, 33 (1921).  
<sup>150</sup> P. DEBYE and P. SCHERRER: *Nachr. Ges. Wiss. Göttingen*, 1916.  
<sup>151</sup> L. W. MCKEEHAN: *Phys. Rev.*, **20**, 424 (1922).



# THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.

SUPPLEMENTARY NOTE.

BY

WILLIAM D. HARKINS, Ph.D.

Department of Chemistry, University of Chicago.

## 83. ATOMIC SPECIES OF ODD ATOMIC WEIGHT.

THE earlier sections of the paper have shown that most of the isotopes of elements of odd atomic number have odd atomic weights and isotopic numbers, while for elements of even atomic number these numbers are even. No general relationship was given in regard to the existence of the much more rare atomic species: those which have an odd atomic weight and isotopic number, associated with an even atomic number. Not only is the number of such atomic species small, but they are also represented in nature by only a comparatively small number of atoms. An empirical relation concerning such isotopic species is made evident by Fig. 3, which plots the atomic number on the X-axis and the isotopic number on the Y-axis. The atomic species of the class in question and below atomic number 38, which have thus far been discovered are:  $^{124}_{11}\text{Be}^{\text{u}}$ ,  $^{12}_{12}\text{Mg}^{\text{u}}$ ,  $^{14}_{14}\text{Si}^{\text{u}}$ ,  $^{34}_{16}\text{Se}^{\text{u}}$ , and  $^{36}_{36}\text{Kr}^{\text{u}}$ . It will be seen that on the plot *each of these atomic species is between two atomic species of the same isotopic number and next higher and next lower atomic numbers*. Thus any isotope of odd atomic weight in an element of even atomic number has the same isotopic number as the adjacent isotopes of elements of odd atomic number, and lies on the same neutronic line (horizontal line in the figure) between them. While not every position of this type is occupied by an atomic species, it is of interest that every atomic species of this class falls in just such a position.

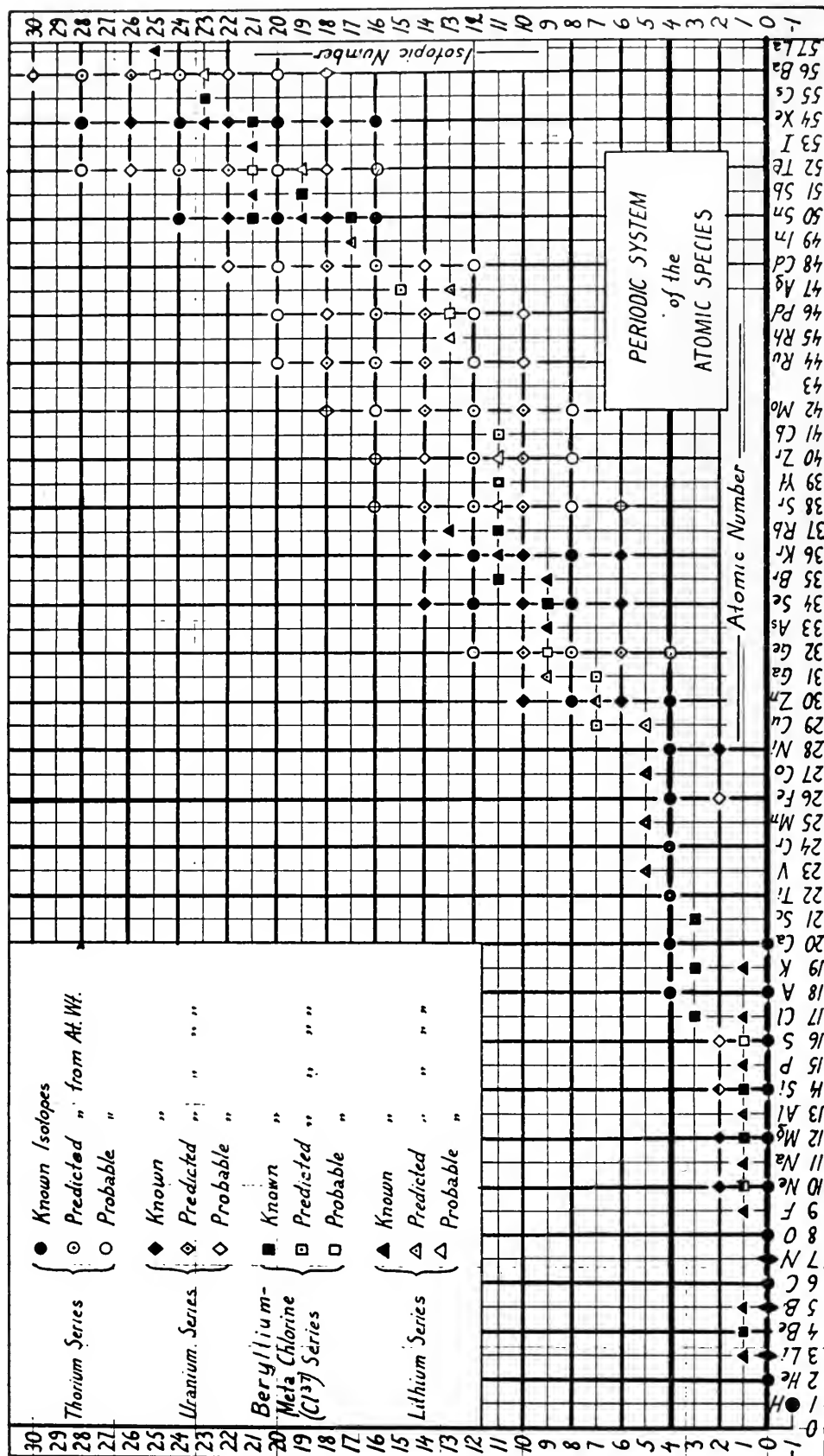
When the atomic number becomes higher the condition for the existence of odd-numbered isotopes of even-numbered elements seems to become less exacting, in that these isotopes occur when there is an atomic species of the same isotopic number existent

---

<sup>124</sup> Here the atomic number is written first, the subscript is the isotopic number and the superscript the atomic weight.



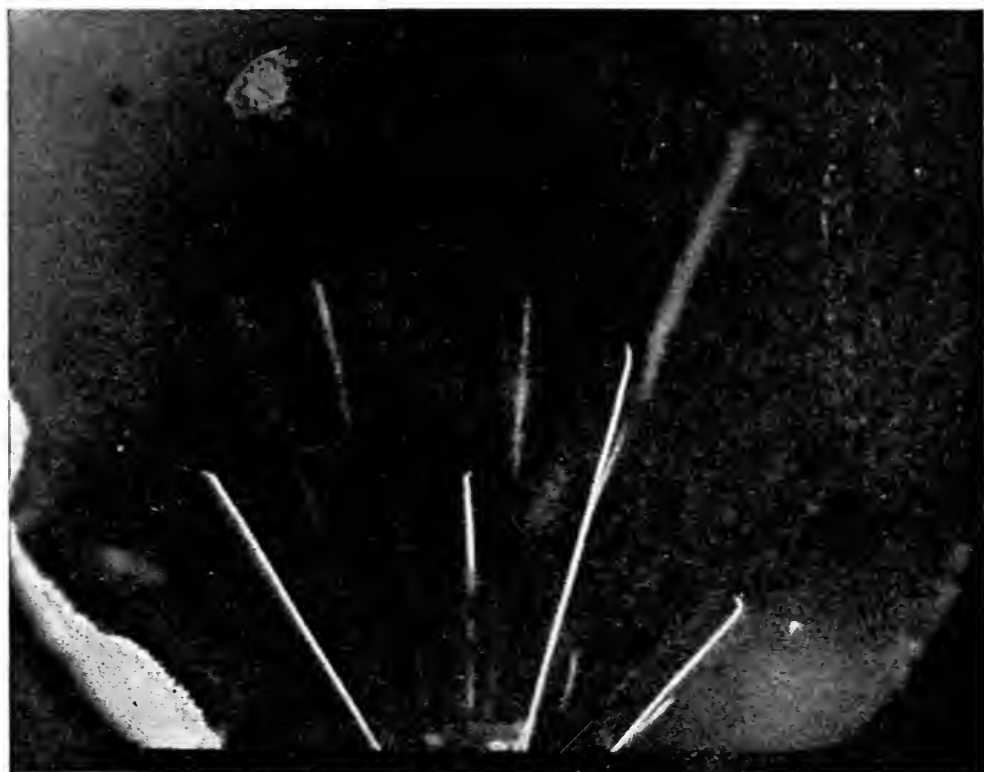
FIG. 43.





in only one, instead of in both of the elements of next higher and lower atomic number. Thus xenon has two isotopes of the class under discussion  $^{129}_{54}\text{Xe}$ , and  $^{131}_{54}\text{Xe}$ . The former of these has the same isotopic number as  $^{129}_{53}\text{I}$ , and the latter, as  $^{131}_{55}\text{Cs}$ . Thus the occurrence of odd atomic weight isotopes of elements of even atomic number is plainly related to the exist-

FIG. 44.



Straight tracks with curves at end.

ence of odd atomic weight isotopes in adjacent elements of odd atomic number.

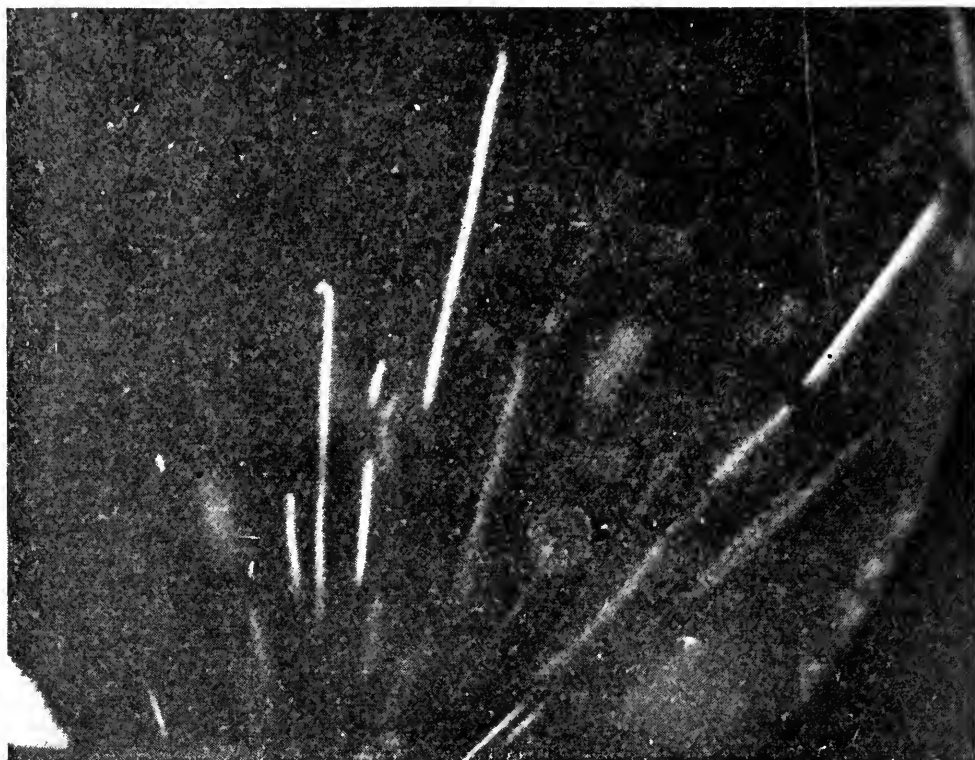
The relation given above indicates the probability of the existence of an isotope of zinc of isotopic number 7, since both of the adjacent elements, copper and gallium, have chemical atomic weights which indicate the existence of an isotope of copper, and one of gallium, of this atomic number. The work of Dempster also shows the high probability that such a zinc isotope exists, since a peak in this position occurs in some of his ionization curves.

Fig. 43 shows that in certain regions every successive corner



along a neutronal line is filled, that is, every possible atomic species exists. This is true along certain lines of odd isotopic number, as isotopic number 1 from sodium to phosphorus. It is probable that elements 31, 32, 33, 34, and 35, all have isotopes of isotopic number 9, and elements 50, 51, 52, 53, and 54, of isotopic number 21. It will be seen that for atomic numbers greater than 28 there are *commonly four or more levels on which atomic species*

FIG. 45.



Straight tracks with one curved at end.

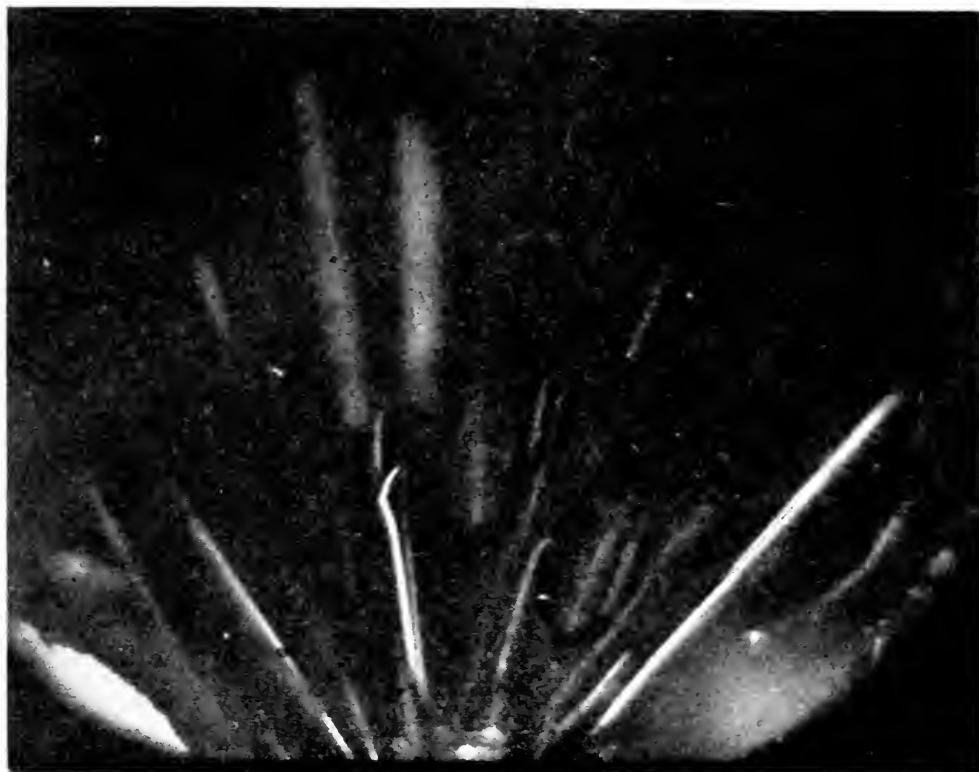
*of even atomic and isotopic number occur, but that usually there is only one level for species of odd isotopic number, except that there are often two levels for elements which give a rise from one level to another. Thus bromine contains the atomic species of highest atomic number which has isotopic number 9, and the atomic species of lowest atomic number in which the isotopic number is 11. There are undoubtedly some isotopes which rise above the common level, as is the case with rubidium of isotopic number*



13. *On the whole the atomic species of odd atomic weight (odd isotopic number) are arranged in the plot in a series of single steps rising from left to right, but occasionally one step lies above another for short distance.*

It is apparent that from helium to lithium of atomic weight 6, and from boron of atomic weight 10 to oxygen, all of which atomic species have an isotopic number zero, the increment in

FIG. 46.



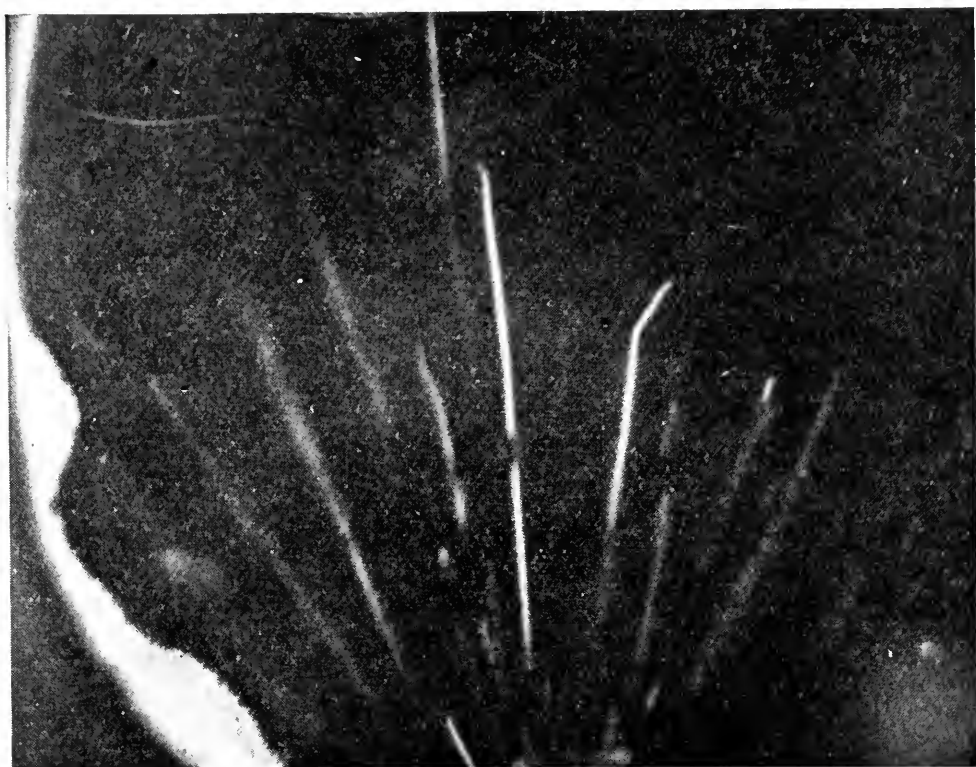
Left turn followed by right turn and a curve.

the composition of the nucleus for an increase of 1 in the atomic number is represented by the formula  $p_2c$ , which is just one-half of an alpha particle ( $p_4c_2$ ). Now the above paragraphs of this section have made it evident that while the increment between nuclei of the same isotopic number is almost always a whole  $\alpha$ -particle when the atomic weight is even, the increment is often only a half  $\alpha$ -particle, or the group  $p_2c$ , when the atomic weight is odd, though in certain other regions it is a whole alpha particle.



This relation calls to mind a suggestion made by the writer several years ago, before this last relation was discovered, to the effect that the group  $p_2e$  may be of fundamental importance in connection with atom building, especially since the formula of any nucleus may be represented as  $(p_2e)_M(pe)_n$ , in which  $M$  is the atomic and  $n$  is the isotopic number. For species of zero isotopic number this reduces to  $(p_2e)_M$ . It might be supposed that the

FIG. 47.



Straight track and track with sharp bend.

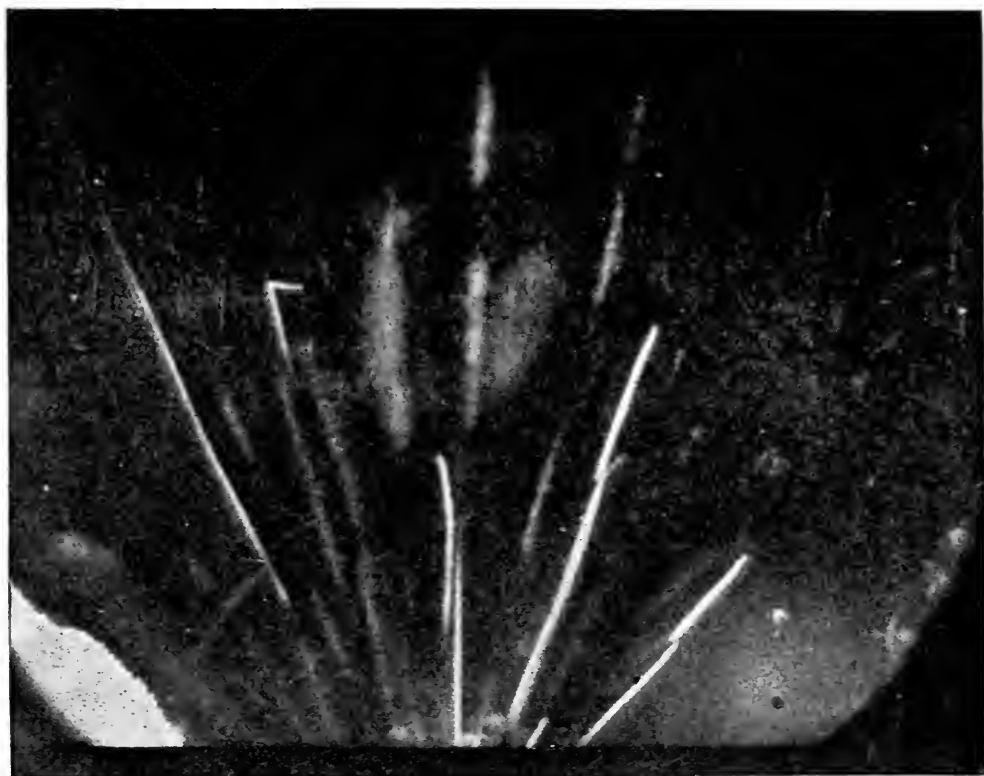
$p_2e$  group is very stable with respect to disintegration, but that in general it does not exist alone, since it readily unites with itself to form a double  $p_2e$  group, or alpha particle, or less often attaches itself to a heavier nucleus. If this is the case, the relation given above would indicate that it attaches itself to a heavy nucleus most easily when the weight of the latter is an odd number. It will be recognized that such suggestions are much more hypothetical than the rest of the material presented in the paper.



## 84. DISCOVERY OF ISOTOPES PREDICTED IN EARLIER SECTIONS.

In the chart <sup>125</sup> of the General System of Isotopes (Fig. 21 between pages 654 and 655) <sup>126</sup> numerous predicted and probable isotopes were listed. It is of interest that since the chart was published the isotopes of antimony and selenium have been detected by Aston, with the result that *for both these elements exactly the same isotopes were found as were listed in the chart.* In the

FIG. 48.



Sharp bend in alpha ray track.

discussion of the chart it was pointed out that no specification was made of the rarely occurring isotopes of odd atomic weight and even atomic number. However, the relation given in the preceding section (Section 83) indicates that the odd-numbered isotope of selenium should be of an isotopic number 9, which corresponds to what was found.

<sup>125</sup> Errors in Fig. 21, Element 7 is specified as H, though it is N, and 52 as Tl, though it is Te.

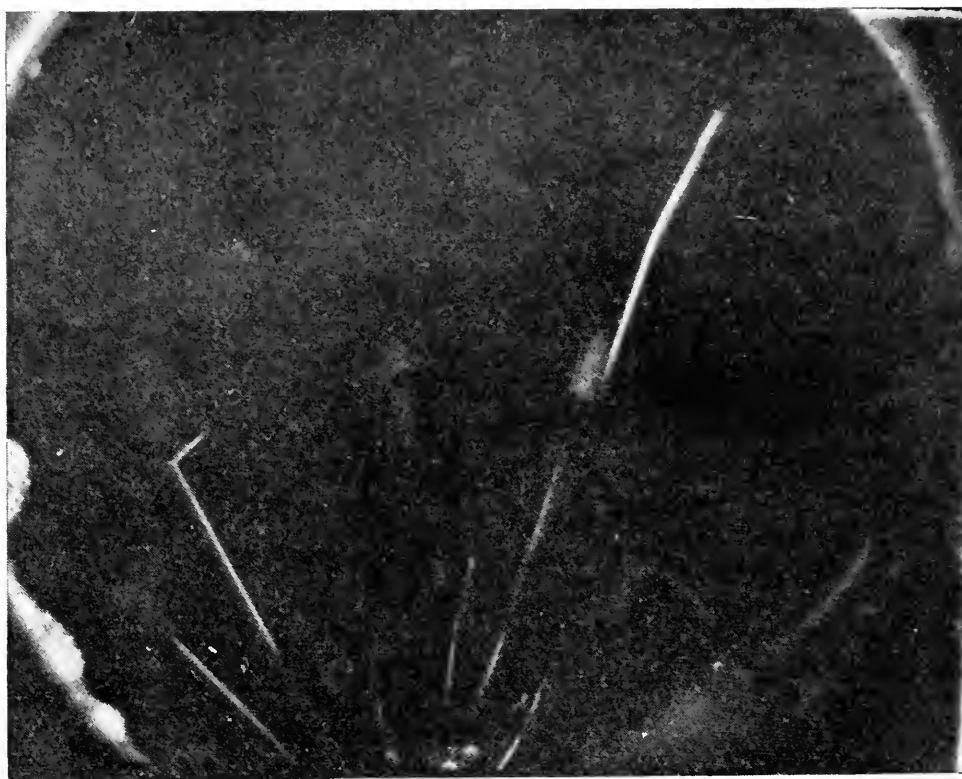
<sup>126</sup> This JOURNAL, Vol. 194, Nov., 1922.



85. RECENT EXPERIMENTAL WORK ON ISOTOPES.<sup>127</sup>

The steel apparatus used by Harkins and Madorsky for the separation of the isotopes of mercury without other cooling than that produced by ice, has given an atomic weight difference of 0.1, while Mulliken in this laboratory has secured the same degree of separation with end samples 22 c.c. each for the light and heavy fractions. In general most of the samples have a

FIG. 49.



Sharp bend in alpha ray track.

volume of 50 c.c. each. The volume of the end fractions is many times larger than that obtained in any previous investigation, and *small* samples of 0.15 unit difference in atomic weight could be obtained from them in about two days of work.

---

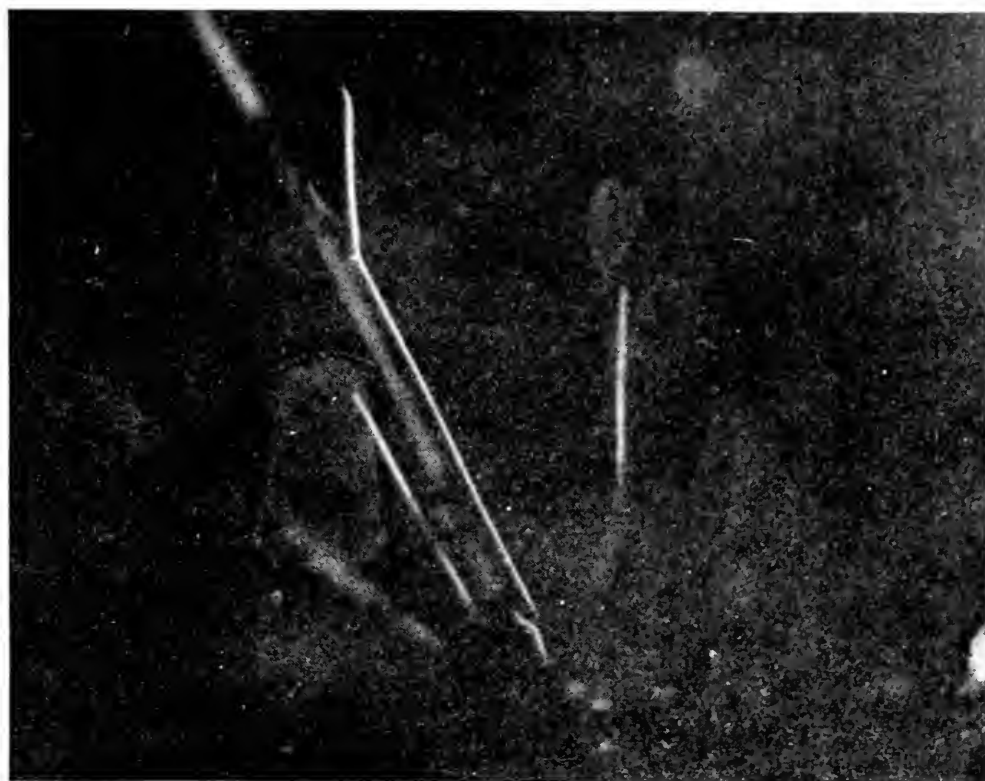
<sup>127</sup> A note in *Nature* of July 14, 1921, states that Bronsted and Hevesy have applied the method of vaporization to hydrogen chloride and have secured a slight separation equal to 0.027 unit of atomic weight.



86. PHOTOGRAPHS OF THE TRACKS OF ALPHA PARTICLES IN GASES,  
BY R. W. RYAN AND W. D. HARKINS.

A few photographs of alpha ray tracks, as obtained in the preliminary work done in this laboratory, were presented in an earlier section of the paper. About ten thousand photographs have now been obtained, and an optical device has been constructed so that two views at right angles can be taken on the

FIG. 50.



Short stub due to nucleus of nitrogen atom and long spur due to alpha particle.

same film. If two motion-picture machines are used at right angles the photographs may be secured upon different films, which gives a brighter image, but has the disadvantage of being twice as costly with respect to film. A large apparatus, which will allow the photographic reproduction of tracks 15 cm. long, is practically ready for use.

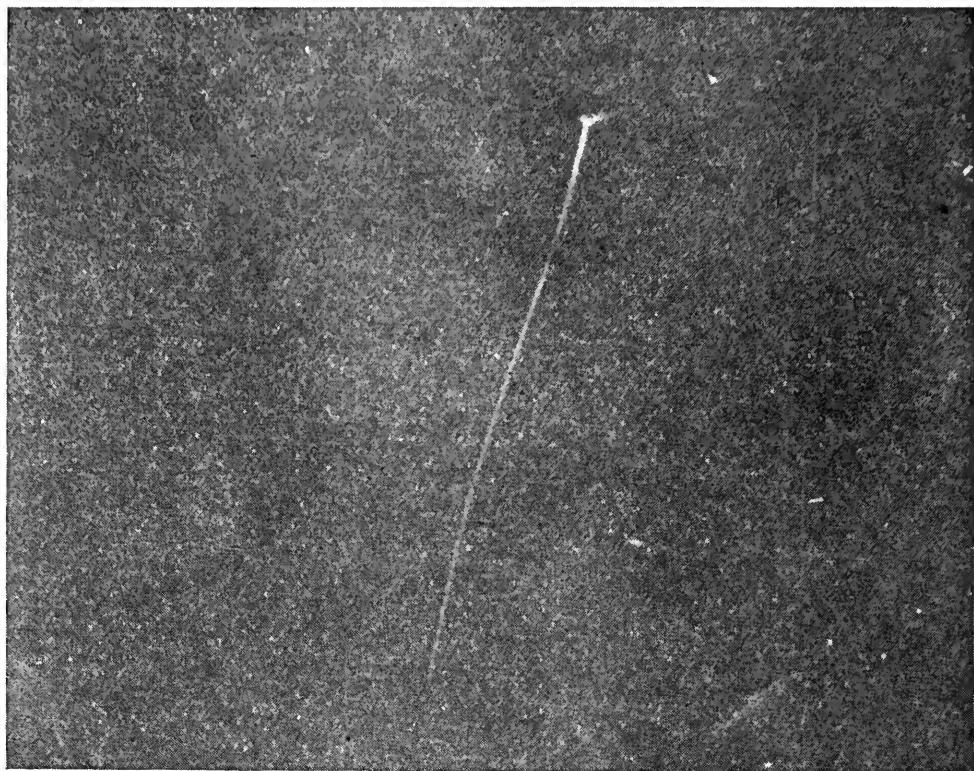
It was noted in an earlier photograph that a track is commonly invisible in a region through which another track has just passed, due to the removal of the supersaturation of the



water vapor, as is shown very markedly in Fig. 39*a*. On this account it is not advisable to use a source which gives too many alpha particles.

Fig. 44 shows four practically straight tracks with curved ends. The curvature at the end is due to the low velocity of the alpha particles at the end of the track, since this gives time for the adjacent atom nuclei to noticeably repel the alpha particles

FIG. 51.



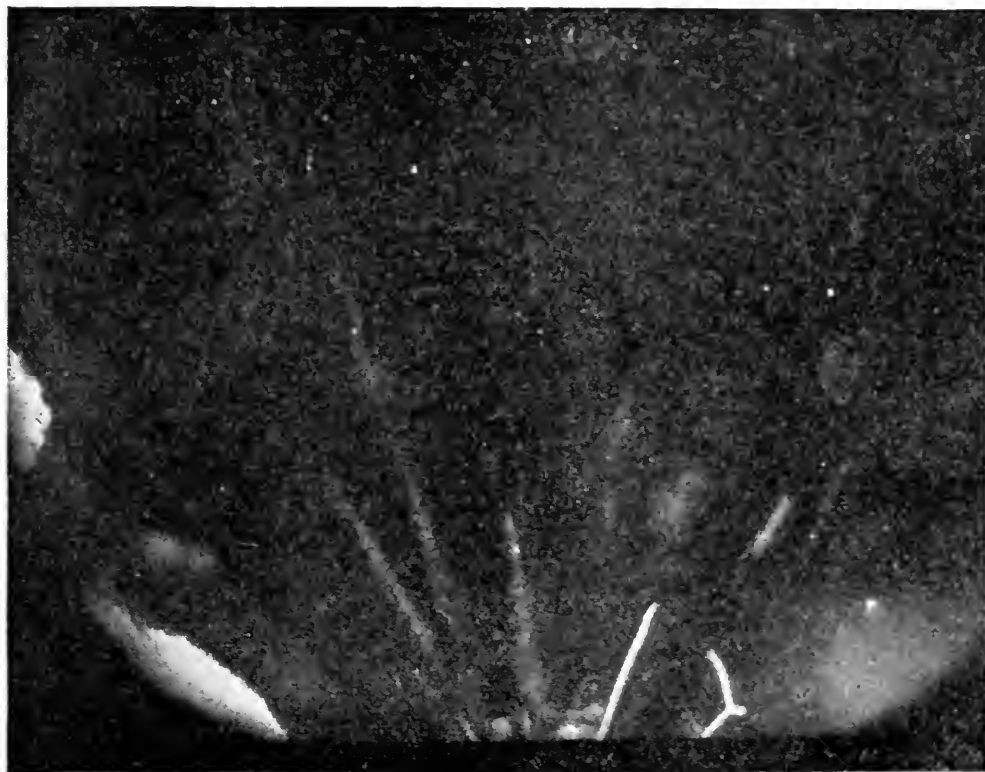
Alpha ray track with double curvature.

and cause what is known as straggling. In Fig. 45 the curvature is particularly great at the end of one of the tracks. A bend toward the left and a later sharp turn to the right, evidently due to a penetration of the alpha particle close to two different nitrogen or oxygen nuclei, may be seen in Fig. 46. The end of this track is evidently influenced by a number of nuclear approaches, since it exhibits a marked curvature. A single sharp bend is to be seen in Fig. 47, and a much sharper one in Fig. 48. A right-angle bend (very nearly), with a slight spur due to the



nucleus of a nitrogen atom, is plainly visible in the photograph from which Fig. 49 is taken. A short stub caused by the nucleus of a nitrogen atom and a long spur, curved at the end, representing the path of the alpha particle after the collision, may be seen in Fig. 50. Fig. 51 is interesting in that it shows a double curvature due to the passage of the alpha particle near two different atom nuclei at a considerable distance apart. This track finally

FIG. 52.



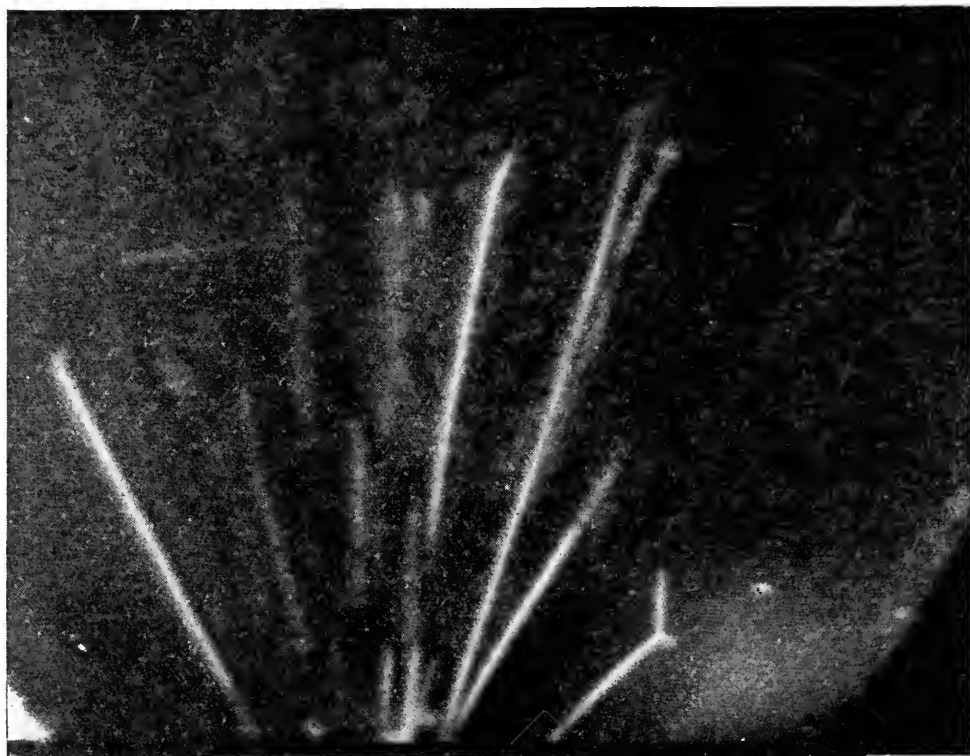
Forked track: One fork due to alpha particle and the other to the nucleus of a nitrogen atom.

ends in a fork due to a very near approach to still another atom nucleus. In each of Figs. 52 and 53 is a fork in which the alpha particle goes in one direction, and the nucleus of the bombarded nitrogen atom in another. Fig. 54 gives a much sharper photograph of a track produced earlier. The fork is nearly in the plane of the picture, the alpha particle being turned through about  $155^\circ$ , while the nitrogen nucleus is hurled forward a considerable distance. In a direct impact the velocity of the rebounding alpha



particle is 0.6, that of a bombarded oxygen atom nucleus 0.4 if the velocity of the alpha particle just before impact is taken as 1, and for a nitrogen nucleus the relations are very nearly the same. A slight straggling of the atom nucleus near the end of its path is indicated by the curve at the end of the track (Fig. 54). Figs. 55 and 56 show tracks in which one limb of the fork is almost a direct continuation of the track of the alpha particle,

FIG. 53.



Same relation as FIG. 52.

while the other branches off at a sharp angle. Bose obtained one such track in hydrogen, so these may represent bombardments against hydrogen nuclei, but more photographs will need to be secured before the origin of this form of fork is made known by the present work. Photographs of the tracks at right angles will be taken in considerable number in the near future. A statistical study of the present set of photographs indicates that the nuclei of nitrogen and oxygen atoms are extremely minute. It is hoped

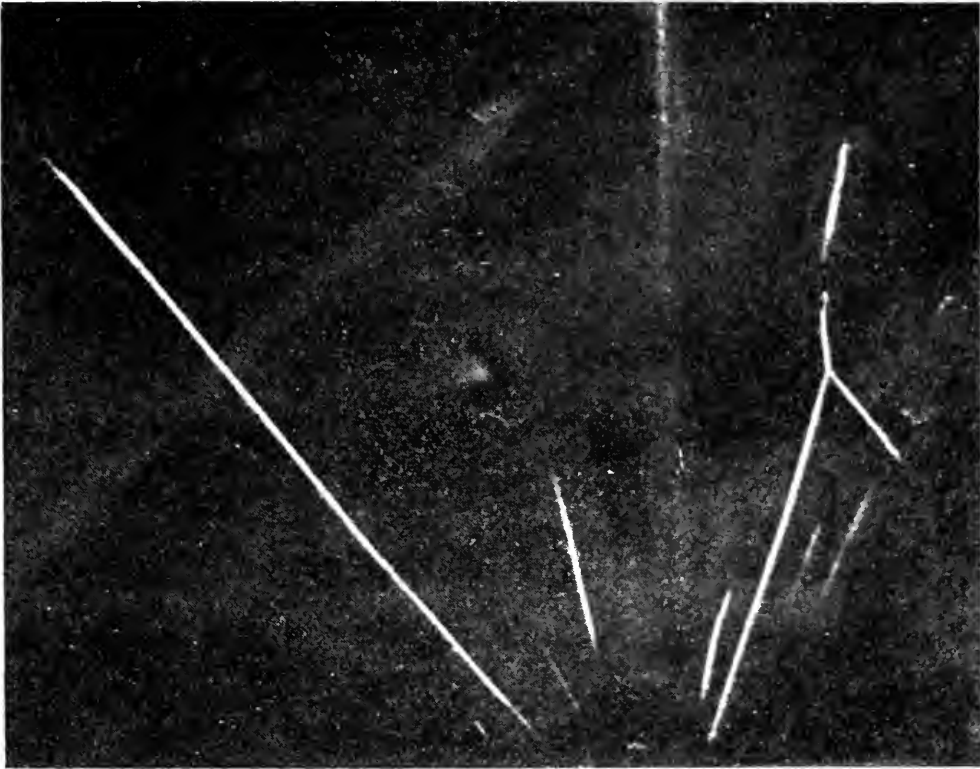


that data on the dimensions of bromine and iodine atom nuclei may be obtained soon.

The photographs show no indication of a disintegration of the bombarded nuclei, so thorium C will be used to give more rapid alpha particles for later work.

Fig. 54 may be used to illustrate what might be expected provided the nucleus which is bombarded by an alpha particle is

FIG. 54.



Forked track showing rebound of alpha particle and forward motion of nitrogen atom.

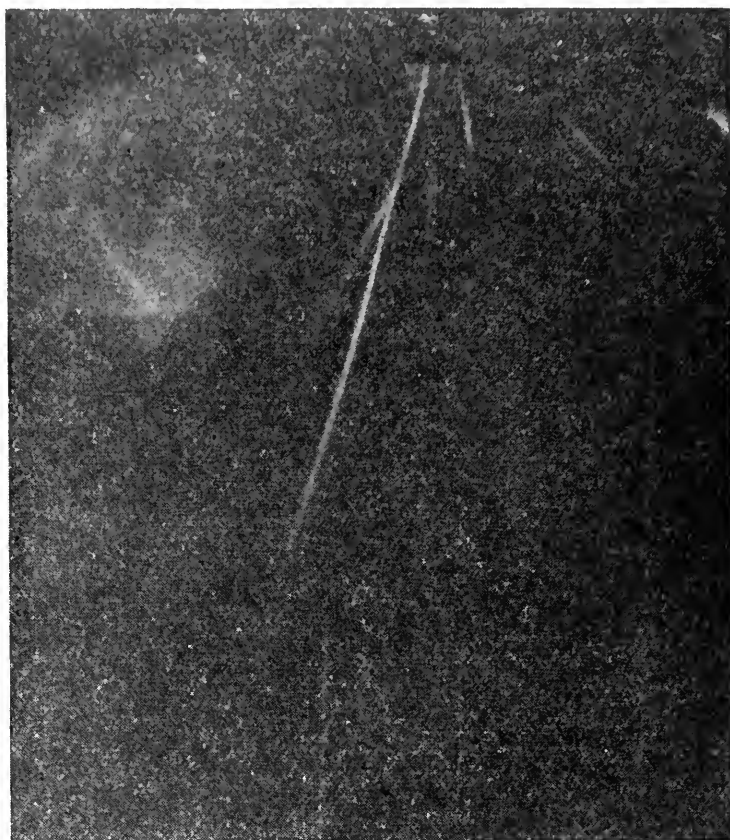
disintegrated. Fig. 54 shows the forward track of the alpha particle, its backward path after the collision, and the forward track of the bombarded nucleus. If the nucleus should disintegrate, then it should give two tracks, one for the heavier, and one for the lighter fragment. In the actual disintegrations thus far obtained the lighter fragment is a hydrogen nucleus of long range. *Thus if a disintegration is secured the original track should split into three branches instead of two.* It is evident, also, that since the disintegrating nucleus would supply energy, there



would not be the simple relation between the angle of incidence and that of reflection exhibited in the figure. Every such disintegration would not be detected, since in some ordinary impacts one of the branches fails to appear.

It is almost certain that the disintegration of nitrogen to give hydrogen could be detected by this means if it were not such a

FIG. 55.



Peculiar fork in track.

rare event in comparison with the number of tracks involved. The writers are preparing to endeavor to make visible the disintegration of aluminum atoms to give hydrogen, which would be much more simple, being only complicated by the effects of the powerful gamma rays given off by the source.<sup>128</sup>

---

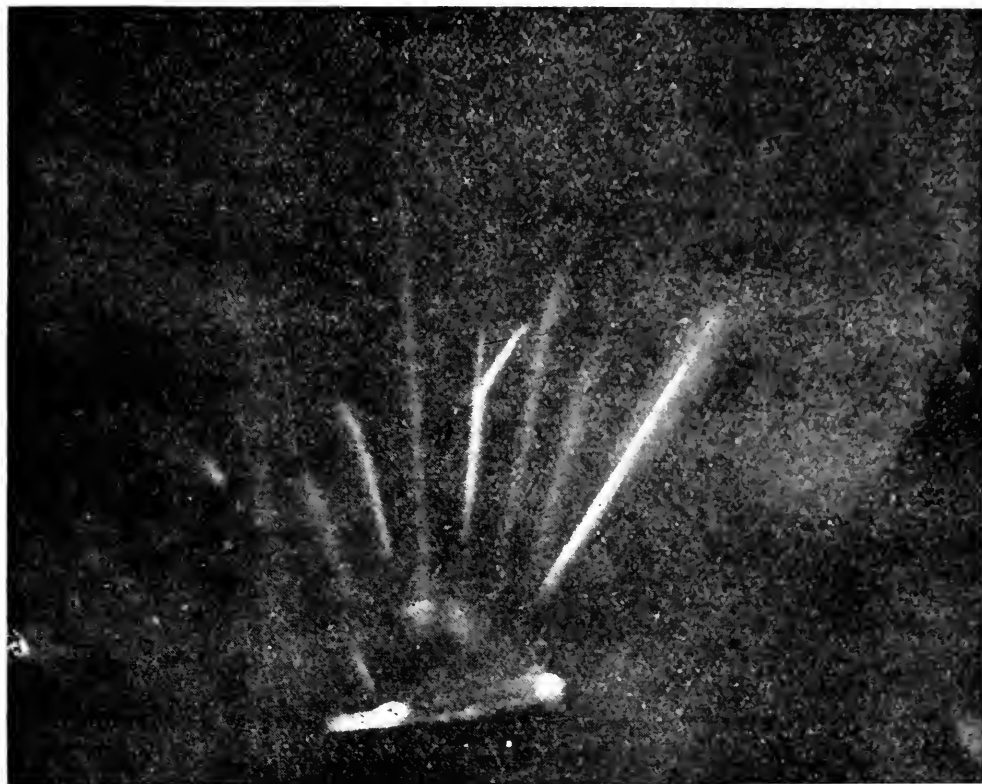
<sup>128</sup> On account of the large demand for lantern slides and copies of the photographs of alpha ray tracks presented in this paper, the writer has arranged with Mr. R. W. Ryan to supply them at a nominal cost, and directly from the original enlargements, since the photographs suffer considerable loss of clearness in reproduction.



## 87. SEPARATION OF ISOTOPES BY GASEOUS DIFFUSION THROUGH A MOVING STREAM OF GAS OR VAPOR.

The diffusion of a gas through a moving stream of another gas, suggested by Mulliken and Harkins<sup>129</sup> under the name of "gaseous diffusion with negative mass motion," has been applied to the separation of helium and neon, which are of course not isotopic, by Hertz.<sup>130</sup> He suggests that the method might be of

FIG. 56.



Split track of alpha particle.

use in the separation of isotopes. In order to get a stream of gas which is easily controlled he uses steam, which may be condensed where it is desired that the flow shall stop, and this improvement is what gives the method its promise. Mulliken has studied the principles of this method and some of his principal conclusions will be given below.

---

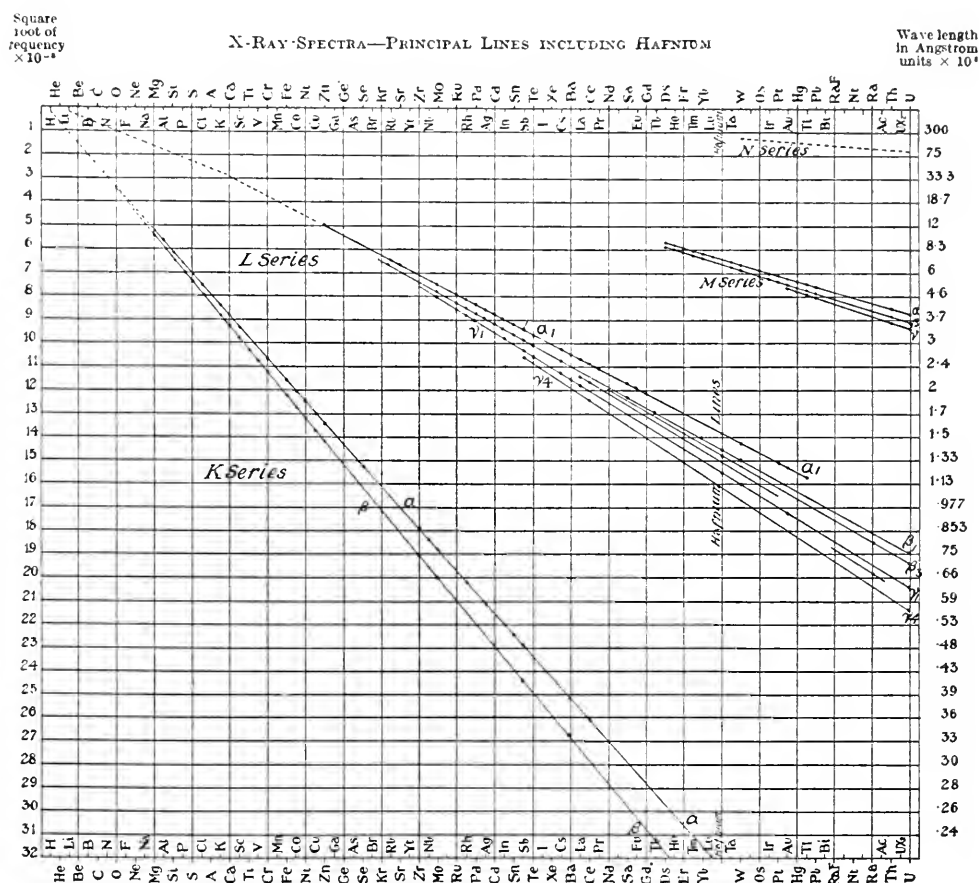
<sup>129</sup> *Loc. cit.*, Jan., 1922.

<sup>130</sup> *Phys. Z.*, Dec., 1922, 23, 433.



Hertz considers his method to be greatly superior to other diffusion methods since it may be made to give any degree of separation in a single operation. However, this can be done in any ordinary diffusion process in the case of the *heavy fraction*. The advantage of the method, therefore, lies in extending this advantage to the light fraction also. Hertz has failed to note that the *rate of production* of either fraction decreases exponentially

FIG. 57.



with the degree of separation of the products, which is just the relation found for the ordinary methods. Thus the rate of production of the light fraction decreases logarithmically as the separation in terms of atomic weight increases arithmetically.

If a steady stream of vapor passes from left to right with a velocity  $v$  across a narrow space between two parallel planes, being supplied constantly at the plane  $X = X$  on the right, and condensed



at an equal rate on the plane  $X = 0$  on the left, then any gas present at a small partial pressure will distribute itself according to the relation  $f = f_0 e^{-\frac{x}{\delta}}$  where  $\delta$  is the diffusion coefficient of the gas, and  $f$  is the fraction of the gas removed at the plane  $X = X$ , which constitutes the light fraction. This is analogous to the relation found for the distribution of a gas in a gravitational field or under centrifugal force.

The difference in the molecular weight produced between the planes is

$$M = (M_2 - M_1) \frac{\left(1 - \frac{\delta_1}{\delta_2}\right) x_1 x_2}{x_1 + x_2 \frac{\delta_1}{\delta_2}} \ln \frac{f_0}{f}.$$

Here  $x$  represents the mol fraction. This equation is given approximately<sup>131</sup> by

$$M = aB \ln \frac{f_0}{f}$$

For molecular diffusion the ratio of the diffusion coefficients of two isotopes is  $\left(\frac{M_2}{M_1}\right)^{1/2}$ , and in gaseous diffusion it is  $\left(\frac{M_2}{M_1}\right)^{1/c}$  where  $c$  is equal to or greater than 2. The value of  $a$  in the above equations is thus equal to or less than 1, since  $a$  is the ratio of  $1/c$  to  $1/2$ . From the formulas given in Jeans ("Dynamical Theory of Gases") the above conclusion that  $c$  is commonly greater than 2 for gaseous diffusion, may be deduced. The value of  $a$  may even approach zero if a gas of high molecular weight, such as mercury, is diffused in a vapor of very low molecular weight, and it should approach the value of one if the molecular weights are reversed, and is probably near  $3/4$  when they are equal. Since in molecular diffusion and in low pressure vaporization the value of  $a$  is one, the lower value in gaseous diffusion is detrimental to the method of Hertz, and to any other method of gaseous diffusion, such as the diffusion of hydrogen chloride into air used by Harkins and Broeker, and Harkins and Hayes. However, the success of the work done by these investigators indicates the utility of the method in spite of the above listed disadvantages.

<sup>131</sup> The equation for the residue in ordinary gaseous diffusion is  $\Delta M = aB \ln C$ , where  $C$  is the cut; for the diffusate it is  $\Delta M = -aB \ln \frac{C}{C-1}$ . Here  $B$  is the separation coefficient previously defined for molecular diffusion or evaporation.



Mr. Herzfeld is testing these conclusions experimentally by working with ordinary gases of widely different molecular weights.

#### 88. SEPARATION OF ISOTOPES BY SYSTEMATIC FRACTIONATION.

The equations which have already been given for the process of diffusion may be easily changed so that they are given in terms of the fraction ( $F$ ) of the material which has passed into the diffused or condensed fractions. Thus for the total diffusate the increase of molecular weight is:

$$(\Delta M)_{TD} = \frac{1-F}{F} E \cdot B \ln(1-F)$$

and that for the instantaneous diffusate ( $ID$ ) is:

$$(\Delta M)_{ID} = (\Delta M)_R - EB = EB [-\ln(1-F) - 1].$$

The total difference in molecular weight between the two fractions produced ( $\Delta\Delta M$ ) is:

$$(\Delta\Delta M) = -\frac{EB}{F} \ln(1-F).$$

Mulliken has recently used these equations to add to the theory of the systematic fractionation of isotopes already presented in Section 78, and a few of the principal results will be outlined here. In planning an extensive separation procedure it is of great importance to be able to estimate the value ( $V$ ) of the fractions produced. At the present time the best that can be done is to estimate this value in terms of the time necessary to produce any fraction or set of fractions by diffusion or evaporation, since this is the only general method which has proved successful. It is found that the value of *any fraction* is proportional to the volume (or number of mols) to the square of the difference between its molecular weight and that of the initial material, inversely proportional to the square of the separation coefficient ( $B$ ), and is therefore proportional to the square of the efficiency of the process. This may be formulated as follows:

$$V = \left(\frac{\Delta M}{B}\right)^2 \cdot Q = \Delta^2 Q, \text{ where } \Delta^2 = \left(\frac{\Delta M}{B}\right)^2$$

since  $\Delta M$  varies as the efficiency ( $E$ ), the value obtained varies as  $E^2$ . This relation holds only when the diffusate is collected in infinitesimal fractions. There is a progressively increasing loss of value as the size of the fractions of the distillate collected is increased. Thus if the fraction in the distillate is 0.1, there is a loss of 0.1 per cent. of the *value* which is almost negligible. The following table illustrates these losses:



TABLE XLV.

*Loss of Value in Collecting Finite Instead of Infinitesimal Diffusate Fractions.*

Fraction in Diffusate = $F$ .	Per cent. Loss of Value for Diffusate and Residue.
0.0	0.0
0.1	0.1
0.2	0.5
0.3	1.3
0.4	2.0
0.5	4.0
1.0	100.0

Thus there is a loss of 4 per cent. in the total value for a cut into two equal fractions ( $F = 0.5$ ). This amounts, however, to a loss of 7.7 per cent. of the value of the diffusate, and a zero loss of value in the residue.

The *value* of an *extreme fraction* may be considered proportional to the time required to build up the entire set of intermediate fractions leading to the desired extreme, and is proportional to the  $e$ 'th power of the separation when  $F = 0.5$ , and approaches the cube of the separation as the fraction in the diffusate becomes smaller.

The rapidity of the attainment of a given extreme separation depends on how much of the value is allowed to remain in the intermediate fractions, and this is larger when the fraction in the diffusate is 0.5, than when infinitesimal fractions are collected, since in the former case the fractions of volume  $Q'$  need to be spaced intervals of  $EB \ln$  two units of atomic weight, while with infinitesimal fractions the same volume  $Q'$  is distributed uniformly over a large range of  $EB$  units of atomic weight. However, notwithstanding its advantages the method of infinitesimal fractions is impracticable, and for general use the cut of two, that is  $F = 0.5$ , seems to give the best general plan of procedure, *especially since it leads to a symmetry of the fractions*.

In general the best design for an apparatus is that which gives a maximum for  $E^3R$ , in which  $E$  is the fractional efficiency and  $R$  is the rate of diffusion (or evaporation).

The time necessary to produce a given change of atomic weight is equal to approximately the  $e$ 'th power of the separation coefficient, provided the diffusion rate and the efficiency can be kept equal in the different processes. Thus a given change in the



atomic weight of zinc could be obtained in one-twenty-eighth ( $1/28$ ) the time necessary with mercury, provided the zinc could be manipulated as simply as the mercury.

In the process of an extended fractionation many fractions are obtained, and it is important to know the loss of value which occurs when they are mixed in order to decrease the inconvenience of handling, which becomes great if this is not done. This loss of value is:

$$-\delta V = (\Delta_1 - \Delta_2) \frac{Q_1 Q_2}{Q_1 + Q_2}$$

If two equal quantities of mercury with a difference of density of 6.3 parts per million are mixed, the loss of value is about 2 per cent. of that obtained in an operation which divides the material into two equal portions. If the difference in density is 10.5 p.p.m. this loss is 5.8 per cent. In general all fractions which do not differ by more than 7 p.p.m. should be mixed in the case of mercury.

In the diffusion of mercury vapor through the walls of a tube of filter paper it was found that the rate ( $R$ ) of diffusion varies directly as about the 1.3 power of the length of the tube, and inversely as about the 1.3 power of the diameter. Thus as the area of the diffusion membrane was *increased* by increasing the diameter of the tube, a seemingly contradictory result was obtained, which was that the total amount of material diffusing through it decreased. This was because the mercury vapor was supplied to the tube at a given rate, and the greater pressure in the smaller tubes more than made up for the smaller diffusion area.

#### 89. THE DISCOVERY OF HAFNIUM.

Five elements of atomic numbers 43, 61, 75, 85, and 87 remain unknown. This is of interest and in accord with the idea of the writer that the odd-numbered elements are less abundant and, in general, less stable than those which are even. In this connection it is important to note the recent discovery of element 72, the last of the elements of even atomic number to be found. In Fig. 24, Section 50, this element is listed as celtium, the last of the rare earths, according to the announcement of its discovery by Urbain and Dauviller. In *Nature* of January 20, 1923, Coster and Hevesy announce the discovery of this element, which they name hafnium, in zirconium minerals, from which they



assume that it belongs to the same group as zirconium. This is in better accordance with the form of the periodic table given in Fig. 24.<sup>132</sup> The element hafnium was discovered by means of its X-ray spectrum, according to the method discovered by Moseley. The lines of the element which were measured belong to the L series and have wave-lengths as follows:  $L_{\alpha_1} = 1.565$ ,  $L_{\alpha_2} = 1.576$ ,  $L_{\beta_1} = 1.371$ ,  $L_{\beta_2} = 1.323$ ,  $L_{\beta_3} = 1.350$ ,  $L_{\gamma_1} = 1.177$  Angstrom units. The relation of these lines to those of other elements is shown in Fig. 57.<sup>133</sup>

#### ERRATA.

1. In Fig. 36 the curve for mercury should be at half the height for that of  $\text{CCl}_4$ .

**A Study of the Deformation of the Photographic Film.**  
CARL BENEDICKS. (*Comptes Rendus*, Oct. 30, 1922.)—In photographing the total eclipse of the sun in 1914, by a mistake the sun's image appeared near the edge of the plate. Later a crack developed at the edge and moved inward until it reached the image of the sun, when it thereupon followed the circular contour. "If, as this unexpected fact makes clear, the light of the sun can cause so considerable an effect, it may be feared that it can cause also a deformation of the sensitive film that cannot be neglected when one is dealing with measurements as delicate as those necessary to be made in order to verify the deviation of light in traversing the gravitational field of the sun." To see whether such a deformation is really caused the following experiment was devised. A glass plate was exposed to powdered bitumen. It was then heated to assure the adhesion of the particles to its surface. It was then photographed. The negative thus obtained had a multitude of sharply outlined white disks. From this a positive was made at the centre of which an artificial sun was produced by letting a circular beam of light fall. This positive represented the plate on which the crack formed and on which distortion might well be produced by the presence of the fictitious image of the sun. Careful measurements showed that no deformation greater than .002 mm. was present. With an objective of focal length equal to 19 feet, such as that used at Sobral in 1919, this would give .07 sec. of arc as the maximum error in the position of a star due to film distortion.

G. F. S.

<sup>132</sup> It may be seen that the remnant of the disc upon which element 72 was marked, is still present in Fig. 24, to the right of the symbol Ta. See McCoy and Terry's "General Chemistry," page 565, for the proper position for element 72, provided Coster and Hevesy's announcement is correct.

<sup>133</sup> *J. Soc. Chem. Ind.*, 1923, 42, 67.



**First Attempt to Teach Conservation of All Natural Resources of a State.**—A forward step in the vital matter of conserving our natural resources has been taken in the preparation of an educational handbook of the resources of Pennsylvania. This book, prepared for use in the Pennsylvania schools to carry out the Smithsonian Institution's purpose of the "increase and diffusion of knowledge among men," presents in novel and striking ways the present situation, causes of waste and how to stop it, and future problems in connection with the conservation of resources. The book will be placed in practically every school in Pennsylvania, and by including the resource material in the geography course, it will be possible to instill into the minds of the school children, the citizens of to-morrow, the necessity of understanding and conserving the resources provided by Nature. While the present handbook is limited to the State of Pennsylvania, there is a nation-wide lesson in it, and such material brought together and placed in the schools of every State would be of immeasurable benefit to the present and future economic condition of the country.

Pennsylvania's primary resource is coal. In this one State is produced 31 per cent. of the country's bituminous and all of the anthracite coal. The chief sources of waste are: Beehive coke-ovens, steam locomotives, which utilize only about 4 per cent. of the energy in coal; heating homes, in which the ordinary coal furnace delivers only about 25 per cent. of the heat energy and unburned coal is dumped into the ash cans. In 200 tests recently made, the average ash can was found to contain 50 per cent. of coal.

In connection with the fullest development of the State's resources there is described the superpower system as proposed by the U. S. Geological Survey. Briefly this system contemplates the standardization of the electrical characteristics of all existing and future electric power plants and transmission lines (in the superpower zone, between Boston and Washington) so as to permit of their interconnection with each other, and so that they will all feed into one huge system of transmission. The great benefits to be derived from this system would appear in the much greater amount of power made available and in a saving of fifty million tons of coal annually.

H. L.

**Chemistry as an Aid in the Detection of Crime.**—The first treatise on toxicology or the science of poisons was written by Orfila and was published during the first quarter of the nineteenth century. Since that time, various chemical methods have been devised, and then utilized for the detection of crime. These methods are reviewed by HENRY LEFFMANN (*Am. Jour. Pharmacy*, 1922, xciv, 691-699). The precipitin test is specific for the blood of man and certain man-like apes. Crystallographic methods serve for the identification of various compounds. Special procedures are used to detect the adulteration of foods and beverages. Physical and chemical tests reveal alterations in, and forgeries of, documents.

J. S. H.



NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

FORMULA FOR THE RATE OF EXHAUSTION OF A LARGE  
TANK BY A RECIPROCATING AIR PUMP.<sup>1</sup>

By E. Buckingham.

[ABSTRACT.]

*Conditions.*—The conditions for the validity of the formula are as follows: (1) The piston and valves do not leak; (2) there is no appreciable throttling except at the valves; (3) the volume to be exhausted is very large in comparison with the piston displacement; (4) the temperature of the air in the tank is constant; (5) the temperature in the pump at the end of any suction stroke is constant; (6) the pump discharges to atmospheric pressure, and the air in the tank starts at atmospheric pressure.

*Notation.*—Let

- $P$  = atmospheric pressure;
- $N$  = number of completed pump cycles;
- $p$  = pressure in tank after  $N$  cycles;
- $x = p/P$  = degree of exhaustion;
- $l$  = limiting or lowest attainable value of  $x$ ;
- $a$  = fraction of 1 atmosphere required to lift the discharge valve;
- $b$  = fraction of 1 atmosphere required to lift the intake valve;
- $c$  = ratio of clearance to piston displacement;
- $t$  = ratio of absolute temperature in the pump at the end of a suction stroke to absolute temperature in the tank;
- $v$  = ratio of volume of tank to piston displacement;
- $n$  = exponent in the equation of the compression line,  $pv^n = \text{constant}$ .

In any one problem the last six quantities are pure numbers and independent of the units used.  $a$ ,  $b$ , and  $c$  are always small; if the valves are operated positively,  $a = b = 0$ ; if the pump is oil sealed,  $c = 0$ . The temperature ratio  $t$  never differs much from unity. The volume ratio  $v$  is supposed to be large. The exponent  $n$  is between 1.0 and 1.4.

---

\* Communicated by the Director.

<sup>1</sup> Technologic Papers, No. 224, price five cents.



*Results.*—The formulas obtained are :

$$N = A \log_{10} \frac{C}{(x-b)^{\frac{1}{n}} - B}$$

and

$$l = B^n + b$$

where

$$A = \frac{2.303 \, n l v.}{1+c}$$

$$B = \frac{c}{1+c} (1+a)^{\frac{1}{n}},$$

$$C = (1-b)^{\frac{1}{n}} - B$$

## AMERICAN AND ENGLISH BALL CLAYS.<sup>2</sup>

By H. H. SORTWELL.

[ABSTRACT.]

THE twenty-one ball clays being used in the largest quantities in the manufacture of china, semiporcelain, electrical porcelain, sanitary ware, and floor and wall tile were studied at the Bureau of Standards. Determinations were made of the water of plasticity and shrinkage relations upon drying, amount of arenaceous material retained by 120-mesh sieves, rate of flow of slips, cohesion of the plastic clay, dry transverse strength when mixed with an equal part of flint, time required for oxidation of carbonaceous material at 750° C., porosity and volume-changes from Orton Seger cone 01 to cone 12, and coloring effect in a standard body.

No great differences were noted in water of plasticity, all of the clays falling within a range of a few per cent. The Dorset clays showed a slightly higher drying shrinkage than the other clays studied. All of the clays showed a tendency to warp in drying, but none developed cracks.

The American clays were much cleaner than the English and contained less coarse mineral matter and dirt which would be removed in lawning the body after blunging. The Kentucky clays were almost free from such material, and the Tennessee clays contained only a small amount, while the English clays were less desirable in this respect.

The transverse strength of equal mixtures of the clays with commercial potters' flint was determined to give a better indi-

<sup>2</sup> Technologic Papers, No. 227, price ten cents.



cation of the comparative bonding power of the clays in a body than would be indicated by the modulus of rupture of the clay alone. The average modulus of rupture of the Tennessee clays tested was 366 pounds per square inch, the Kentucky clays averaged 282 pounds per square inch, the clays from Dorset, England, 405 pounds per square inch, the Devonshire clays 443 pounds per square inch, and English clays, whose exact source was not known, 419 pounds per square inch. In general the English clays were stronger than the domestic, but two of the American clays compared favorably with the average English clay.

From the results obtained the rate of flow of slips from the efflux viscosimeter did not appear to be a valuable criterion of the inherent plastic qualities for use in comparing ball clays. Soluble salts in the clays probably affect the results.

The cohesive strengths of the plastic clays were determined at different water contents and are shown graphically. These results showed no distinctions which compared with the value of the clays for jiggering as judged by practical potters.

Some of the English clays are very high in carbonaceous matter, eleven hours being required in two cases to completely remove the black core from specimens  $1\frac{1}{4}$  by  $1\frac{1}{4}$  by 2 inches. The clays from Devonshire as a class required the longest time for oxidation. The Dorset clays and those from Tennessee contained a moderate amount of carbonaceous matter, while the Kentucky clays contained but little. It was noticed that there was a relationship between the amount of carbonaceous matter and the strength when dry, the more carbonaceous clays usually being stronger.

The burning behavior of the American and English clays was radically different. The English clays vitrified at a low temperature and remained almost constant in porosity and volume up to cone 12. No evidence of overburning was noticed at that temperature. There was some variation in the burning behavior of the clays from Devonshire, but the Dorset clays underwent practically the same changes in firing. The American clays showed a gradual reduction in porosity from cone 01 to cone 12. Tennessee ball clay No. 5 was the only domestic clay which vitrified at cone 8. Tennessee No. 3 matured at cone 10, and Tennessee No. 11 and Kentucky No. 4 at cone 12. The other two Kentucky clays studied were not vitrified at cone 12. Throughout the firing



range studied the American clays were constantly changing in volume.

In the standard body the Tennessee clays as a class showed the best color. The Kentucky and Devon clays were fair in this regard while the Dorset clays were comparatively poor in coloring effect.

Although the English clays have a more desirable firing behavior and greater strength when dry, the American clays contain less material to be removed in body preparation, contain less carbonaceous matter which may lead to trouble in firing, and burn to a better color in the body. Because of their better color they may be used in larger quantities, thereby overcoming in a measure their lower strength. With a slight adjustment in flux content of the body they may be successfully used to replace the English clays.

All of the results are given in tabular form and graphically when feasible. A detailed description of each individual clay is given, and a classification of ball clays based on their properties has been drawn from the results of the work.

---

**The Rotation of the Plane of Polarization of Electromagnetic Waves Produced by a Three-dimensional Grating.** K. F. LINDMAN. (*Ann. der Phys.*, vol. 69, p. 270, 1922.)—A few years ago this Finnish physicist showed by experiment that when plane polarized Hertzian waves pass through a system of spiral electrical resonators their plane of polarization is rotated in accordance with a theory advanced by Drude. Later he found further that an assemblage of a large number of left-wound resonators, arranged at random in space, and thus constituting a three-dimensional grating, would rotate to the right or to the left the plane of the polarized wave passing through, according to whether the wave-length of the incident wave was longer or shorter than that of the wave corresponding to the resonators.

In this paper he tests a formula given by Natanson for the case just described, and finds excellent agreement. The wave-length of the incident waves was varied so as to be in part longer and in part shorter than the characteristic wave-length of the resonator, 19.2 cm. The following list gives first the wave-length of the incident electrical radiation, then the angle through which the plane was rotated upon passage through the space grating; 34.2 cm.,  $5^\circ$ ; 26 cm.,  $11^\circ$ ; 22.8 cm.,  $16^\circ$ ; 20.0 cm.,  $10^\circ$ ; 19.2 cm.,  $0^\circ$ ; 15.4 cm.,  $-22^\circ$ ; 12.2 cm.,  $-16^\circ$ .

G. F. S.



## NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.\*

### FILM DISTORTION AND ACCURACY OF PHOTOGRAPHIC REGISTRATION OF POSITION.<sup>1</sup>

By F. E. Ross.

THE results of the investigations by Schlesinger, Perrine, and Albrecht are summarized. In this investigation photographs of artificial stars were made with a precision camera reducing in the ratio of 1 to 20, on plates one inch wide pressed firmly against a rigid metal frame. In agreement with previous results, no evidence of systematic errors in distance was found, indicating that, in general, distortions are of purely local origin and extent. While the average measurements of ten exposures on a triple-coated plate are practically the same as for ten exposures on a thin emulsion, the local distortions are greater on the thick film. Yet the greatest variation from the mean was only 0.0044 mm. Faint and normal exposures gave the same average measurements within 0.0003 mm. Examination of the images showed that the effects of local variations in distribution of the silver bromide grains and of variations in sensitiveness and in development are negligible. Intensification modifies the minor details of image structure, but does not remove the larger irregularities in the original images nor change the centre of gravity appreciably. Measurements of the same plates, when wet and dry, agree accurately and indicate that, on drying, the images move perpendicular to the surface. However, this is not the case for images within a few millimetres of the edge, as these move outward on drying with alcohol or by hardening with formalin. It is concluded that the principal factor in producing the slight image displacements observed is local non-homogeneity of the gelatin. The probable error in accuracy of measurements of the position of stellar images is found to be considerably less in the case of plates with a fine grain thin emulsion (astronomical) than for those with thicker emulsions (Seed 30 and triple-coated). Intensification of weak

---

\* Communicated by the Director.

<sup>1</sup> Communication No. 154 from the Research Laboratory of the Eastman Kodak Company and published in *Astrophys. J.*, January, 1923, p. 33.



images also decreases the error. In the foregoing measurements the probable error of a single setting was about 0.0005 mm. whereas displacement due to film distortion varied up to 0.002 mm. as a maximum, but averaged only 0.0005 mm. for normal exposures on the thin emulsion.

---

**Food Requirements of Man.**—The Food (War) Committee of the Royal Society has published a report on the food requirements of man and their variations according to age, sex, size, and occupation. On account of refuse and waste, the food as purchased should contain approximately 10 per cent. more utilizable calories than are actually required by the individual. The energy requirement of a man varies with the work performed, and ranges from 2500 to 5000 calories daily; it may rise as high as 6000 or even 8000 calories daily in exceptional cases such as the Canadian lumbermen in winter. The average working woman requires 2400 calories of energy daily; women engaged in sedentary labor, such as typewriting, require only 1900 calories daily. Brain workers require from 2200 to 2600 calories daily; their diet should be relatively high in protein. During exposure to low temperatures, extra energy should be supplied as protein (meat or fish) to those engaged in sedentary occupations, and as fat to those engaged in bodily work. Children under six years of age have 50 per cent. of the food requirement of an average man, those between six and ten years 60 per cent., and those between ten and thirteen years 83 per cent. of that requirement; those over thirteen years of age require the same amount of food as an adult of the same sex. A growing child working with the same energy as an adult man requires approximately 200 additional calories daily.

The diet of an average man should contain at least 70 or 80 grams of protein daily, a portion of which should be of animal origin. Milk should serve as a source of protein in the diet of infants and young children. The minimum amount of fat required daily varies with the race, from 20 grams in the case of a Japanese soldier to 75 grams in the case of people of British descent. From 35 to 40 per cent. of the total energy requirement of the body may be supplied as fat; those engaged in vigorous muscular work should receive at least 25 per cent. of their energy intake in the form of fat. A certain amount of fresh fruits or green vegetables should be eaten to supply the requisite vitamins. The diet should also include carbohydrates and salts.

A condition of semi-starvation, with the food intake reduced to two-thirds its normal value, apparently can be endured for a period of several months without danger to health, but gives rise to a greatly reduced resistance to tuberculosis if extended over a period of several years.

J. S. H.



## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

### CONPHASEOLIN.<sup>1</sup>

A NEW GLOBULIN FROM THE NAVY BEAN, *PHASEOLUS VULGARIS*.

By Henry C. Waterman, Carl O. Johns and D. Breese Jones.

[ABSTRACT.]

FRACTIONATION of a 2 per cent. aqueous sodium chloride extract of the navy bean, *Phaseolus vulgaris*, with ammonium sulphate as the precipitant, separated the protein content of the extract into two principal fractions. One of these was identified with the phaseolin previously described by Osborne, but the other the  $\alpha$ -fraction in ammonium sulphate precipitation, proved to be a hitherto unknown globulin, having a chemical composition which differentiated it sharply from both of the proteins (*phaseolin* and *phaselin*) isolated by Osborne. The name *conphaseolin* has been assigned to the new substance. It is distinguished from phaseolin and phaselin by its very much higher sulphur content. In nitrogen and in carbon content also, however, as well as in certain of its physical properties, it is notably different from either of the two proteins with which it is associated.

Conphaseolin is an  $\alpha$ -globulin of the same type as those previously found in the lima, mung and adzuki bean. It has the typical general properties of the group. It is precipitable by ammonium sulphate at a relatively low concentration, is readily denaturable, and possesses a high carbon content and a very high sulphur content. The lysine figure, 10.69, is the highest which has thus far been found for any vegetable protein.

### CHRONIC INTOXICATION BY SMALL QUANTITIES OF CADMIUM CHLORIDE IN THE DIET.<sup>2</sup>

By Carl O. Johns, A. J. Finks and Carl L. Alsberg.

[ABSTRACT.]

VARIOUS concentrations of cadmium chloride were incorporated in a diet which was known to be adequate for the normal growth of rats. Diets containing from 1000 to 62.5 parts per million of cadmium were tested. Very little or no growth

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *J. Biol. Chem.*, Feb., 1923, **55**, 93.

<sup>2</sup> Published in *J. Pharmacol.*, Feb., 1922, **21**, 59.



occurred and death ensued when the concentration of cadmium was 1000, 500, or 250 parts per million. When there were 125 parts per million of cadmium in the diet, the initial rate of growth was normal. All of the male rats receiving this concentration of cadmium died in about fifty days, while the majority of the females survived a very much longer time, one of them dying at the end of 199 days, while another was still living at the end of 280 days.

A concentration of cadmium of 62.5 parts per million had no effect on growth, the rate of growth and food intake being normal. The food intake increased as the concentration of cadmium in the diet was decreased. Whether the interference with growth was due solely to the diminished food intake was not determined. With a dosage of 0.56 mgm. of cadmium per day no cumulative action was observed.

---

**STUDIES ON THE PHARMACOLOGY OF CADMIUM  
AND ZINC WITH PARTICULAR REFERENCE  
TO EMESIS.<sup>3</sup>**

**By Erich W. Schwartz and Carl L. Alsberg.**

[ABSTRACT.]

ZINC, calculated as the metal, is about equally toxic for all species studied (rats, rabbits, cats and dogs) when injected intravenously. Cadmium is about three times more toxic to cats and dogs, but to rabbits and rats four or five times more toxic than zinc.

On oral administration the lethal dose of zinc is from five to seven times greater than that of cadmium. In dilute solutions used, cadmium is more toxic than in more concentrated solutions.

The consumption of an average-sized meal of raw hashed meat containing 350 to 400 parts per million of cadmium or 3000 parts per million of zinc is almost always followed by emesis. Cadmium calculated as the metal is eight to nine times more effective as an emetic than zinc.

Concentrations of cadmium of 250 or more parts per million in the diet are incompatible with life. This is also the mean emetic concentration. Recovery followed reduction of this concentration. No evidence of cumulative systematic action was

---

<sup>3</sup> Published in *J. Pharmacol.*, Feb., 1922, 21, 1.



obtained in these experiments. However, slight loss of appetite, nibbling of food and occasional vomiting indicate that, although apparently compatible with life, the presence in the food of the lower concentrations tried is decidedly objectionable.

No evidence of storage of cadmium other than in the kidney, liver and spleen was obtained. The kidney usually contained the greater part; the spleen contained the least and sometimes none.

---

**Vertical Movements of the Atmosphere with Overcast Sky and the Connection between Cloudiness and the Velocity with which Depressions Travel.** G. REBOUL. (*Comptes Rendus*, December 4, 1922.)—The existence of ascending currents of air explains very readily the formation of cumulus clouds. On the other hand, there are meteorologists who regard the condensation of water vapor in the higher regions of the atmosphere as the chief cause of ascending currents. No matter which view may in the end prove to be the correct one, it is of interest to investigate experimentally the connection existing between cloudiness and the velocity of the ascending air currents. The usual method of following a balloon in its upward flight by means of a theodolite breaks down in cloudy weather because the clouds interfere with the sight of the balloon. The Geographical Service of the French Army toward the end of the war had established stations for exploring the air in cloudy weather. For some months such a station was conducted by Mr. Reboul, who availed himself of the opportunity to investigate the question at issue. Acoustical methods were used to indicate the successive positions of the ascending balloons, which usually attained an elevation of from 5000 to 6000 metres. In all, 270 ascensions of small balloons were made. In working up the results comparison was made between the velocity of ascent under a certain kind of sky and the normal velocity, allowance being made for the size of the balloon employed. "These results show very definitely that, when the sky is clear or only slightly cloudy, the balloon mounts with a velocity less than the normal. On the other hand, when the sky is overcast or very cloudy the balloon ascends with a velocity greater than the normal. In this case there are surely ascending currents. When there is rain the effect of the ascending currents is opposed evidently by the shock of the drops on the balloon and by the additional mass of the water adhering to it."

According to Helmholtz, when there are ascending currents, atmospheric depressions can travel more quickly. Applying the results just given, it should likewise follow that atmospheric depressions travel more quickly in cloudy than in clear weather. This conclusion is confirmed by an examination of the quotients got by dividing the mean velocity of depressions in Western Europe in each season of the year by a number designating the cloudiness at



Paris during that season. The four quotients are close together, thus showing that a high velocity of travel is likely to be found when there is much cloudiness. The importance of this relation in predicting the weather is obvious. G. F. S.

**Cathode Disintegration.** THE RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LTD., London. (*Phil. Mag.*, Jan., 1923.)—In order to minimize difficulties in the interpretation of results the discharge in a triode with a thermionic cathode was used. The anode was a nickel plate, the cathode a tungsten spiral heated by a 6-volt battery, while the grid, lying between them, consisted of a close spiral of fine tungsten wire. "The current to the grid, when the grid is negative to the cathode, is then a measure of the number of positive ions arriving at it, and the speed of the ions arriving is related comparatively simply to the potentials of the electrodes."

The loss of mass in the grid was determined by measuring its increase of resistance due to disintegration. "A change in conductivity amounting to one three-thousandth part of the grid in its initial condition could be detected; this corresponds to a loss of weight of about .0024 mgm."

It was found that for disintegration to take place positive ions must strike. When the grid was an anode, it lost no mass at all. Furthermore, the temperature of the grid makes no difference to the disintegration, at least within the range  $200^{\circ}$  to  $1200^{\circ}$  C.

The relation between the number of atoms of tungsten lost and the number of positive atoms striking the grid was calculated. This ratio is always a proper fraction, in a few instances exceeding .5. With the same difference of potential maintained in all cases between the anode and the grid this ratio varies greatly with the nature of the surrounding gas. It is least with hydrogen, then follow in ascending order, helium, nitrogen, a mixture of helium and neon, mercury vapor and argon. The highest value found for it was about 100 times the smallest.

In all cases, except with argon, disintegration is accompanied by a decrease in the pressure of the gas. "The gas disappears slowly, being absorbed in, or on the surface of, the metal deposited on the walls." "Nitrogen probably disappears most rapidly and helium least rapidly." G. F. S.

**A New Radioactive Mineral, Parsonite.** A. SCHOEP. (*Comptes Rendus*, January 15, 1923.)—With the compact green masses of chalcocite from the Belgian Congo there are found several uraniferous minerals of yellowish color. Along with these an additional mineral has recently been recognized. It occurs in small, pale-brownish crystals of specific gravity 6.23 and of index of refraction 1.99. Its composition seems to be  $2\text{PbO} \cdot \text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . The radioactive constituent,  $\text{UO}_3$ , forms 32.59 per cent. of the whole. The mineral has been named after Professor Parsons of the University of Toronto. G. F. S.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

### LIGNITE CARBONIZING EXPERIMENTS.

By W. W. Odell.

As the result of experiments conducted by the Bureau of Mines and the University of North Dakota, a lignite carbonizer, simple in construction and operation, and with a relatively very low first cost, has been devised. This oven was developed to fill the need for an oven which can be cheaply built and intermittently operated by lignite mine owners, yielding a char which can, if desired, be used as fuel without further processing.

By-products—gas and tar—are not recovered in the operation of this carbonizer, but with certain alterations in design they may be recovered, although they probably will not be as valuable as the by-products from other carbonizers are usually rated. The carbonizer may be operated intermittently without serious damage to it. Lignite char can be made at a much lower cost (approximately \$1.25 per ton less) in this oven than in the by-product ovens hitherto suggested for carbonizing lignite. This is chiefly due to the large capacity and low cost of the carbonizer. Details regarding this lignite carbonizer are given in Serial 2441, of the Bureau of Mines, Department of the Interior.

Following the favorable tests on lignites of North Dakota, by the Bureau of Mines in coöperation with the University of North Dakota, arrangements were made for operating the vertical carbonizing oven at Grand Forks, North Dakota, using Canadian lignite. The present work is being done in coöperation with the Canadian Lignite Utilization Board, in order to determine whether the oven is suitable for the treatment of Canadian lignites. A large-scale test of Canadian lignite was so satisfactory that the board has decided to erect a Bureau of Mines oven at its experimental plant at Bienfait, Saskatchewan.

### CONDENSATION LOSSES OF WATER GAS.

By W. A. Dunkley.

THE Central District Experiment Station of the Bureau of Mines at Urbana, Illinois, recently undertook a study of condensation losses due to the transmission of carburetted water gas

---

\* Communicated by the Director.



under high pressures in the distribution system of the Western United Corporation of Aurora, Illinois. The most distant distributing point on the system is at Harvard, Illinois, about eighty-five miles from the plant. The territory supplied is approximately eighty-five miles long and thirty-five miles wide, the total mileage of mains being 1223, or approximately 24 per cent. of all the gas mains in Illinois outside the city of Chicago. With so extensive a distribution system and so high an initial pressure, it is not surprising that the unaccounted-for gas, or excess of production over sales, should be higher than in a small low-pressure system. In a fairly good system of the latter type, the excess of production over sales is seldom less than 5 or 6 per cent. and instances are by no means uncommon where the unaccounted loss is double this figure. In the Western United System the unaccounted-for gas for a time was in the neighborhood of 20 per cent. Details of the investigation are given in Serial 2447 of the Bureau of Mines.

---

#### **YIELD AND QUALITY OF BY-PRODUCTS FROM FREEPORT COAL.**

**By Joseph D. Davis.**

A STUDY of the yield and quality of the gas, oil and other constituents of the Freeport coal-bed in Pennsylvania has been completed by the U. S. Bureau of Mines in coöperation with the Carnegie Institution of Technology and with mine operators and engineers. This investigation was undertaken in order to obtain data on the possibility of recovering from the cannel and bone of this coal-bed, oils and other by-products as can be done with oil shales. The tests show that the cannel coal yields 27 to 33 gallons of tar oils, 3800 to 4500 cubic feet of gas, 9 to 10 pounds of ammonium sulphate, and 75 per cent. of a rather high-ash smokeless fuel per ton of raw material carbonized at low temperatures. It is possible that in the relatively near future this cannel coal, now wasted, can be commercially treated at a profit, but it is doubtful whether bone coal can be so treated. The time when utilization will become economical depends on the rate of diminution of petroleum resources. The complete details have been published as Bulletin 1 of the Carnegie Institution of Technology.



**SPONTANEOUS COMBUSTION OF BITUMINOUS COAL.**

By Joseph D. Davis.

SAFE storage of bituminous coal, which is probably the only solution of stabilizing the coal industry, involves means to overcome hazards of spontaneous ignition when coal is stored in large piles. On account of the divergence of opinions and the variety of methods proposed for storing coal, the Bureau of Mines, in coöperation with the Carnegie Institution of Technology, has conducted a laboratory study of the factors involved in spontaneous combustion of bituminous coal. One of the principal objects was to determine why some coals ignite more readily than others.

A laboratory test was devised for determining the relative tendency of coals to fire spontaneously, and this "critical temperature" test was applied to many coals. The conclusions reached as a result of this study are that fine coal dust and moist air quickly increase the hazards of spontaneous combustion. Coal finer than 200 mesh has a critical temperature of  $171^{\circ}\text{C}$ ., while coal between 10 and 20 mesh has a critical temperature of  $231^{\circ}\text{C}$ . Coal coarser than one-fourth inch showed no rapid self-heating. Therefore, the presence of fines in a coal pile should be avoided. Moisture in the air or coal facilitates oxidation and consequent heating. Pyrite in lump form has no dangerous effect in coal.

Mixtures of fresh and partly oxidized coal heat no more rapidly than fresh coal. The "anthraxylon" or "woody" constituents of the coal have a lower critical temperature than the "attritus" constituents, but more investigation is needed to evaluate the readily oxidizable constituents in coal and thus determine which are the more responsible for spontaneous heating. The critical-temperature method evolved for testing coals seems suited for grading their relative tendencies to fire spontaneously, and the Bureau of Mines expects to develop this method further and apply it in a survey of the coals of the United States. Further details will be found in the recent report on this subject, which was published as Bulletin 3 of the Carnegie Institution of Technology.

---

**The Evaluation of the Colors of the Spectrum in Terms of the Three Primary Colors.** R. A. HOUSTOUN. (*Phil. Mag.*, Jan., 1923.)—"If we take three colors—a red, a green, and a blue—and represent them by the corners of an equilateral triangle, then any



color whatever can be represented by a point in the plane of the triangle. Any color obtained by mixing two colors is represented by a point on the straight line joining these two colors which divides the distance between them inversely in the ratio of their intensities. That is, to find the position of the mixture we regard the colors as particles the masses of which are proportional to their intensities, and proceed to find the centroid of these particles." All the colors that can be obtained by combining in any proportions the three primary colors have locations within the triangle.

Determinations of the composition of colors according to this plan have been made by several experimenters. Four years ago Doctor Houstoun worked over their results so as to express them in the same units and found that considerable divergences existed. He has now devised a new method of comparison and has made an independent series of determinations. He has learned, moreover, why his predecessors failed to agree among themselves. "As a result of our investigation, we are of the opinion that this is because the subject does not admit of very exact measurement; besides the differences which occur between different observers, the measurements made by the same observer vary somewhat from time to time." "Of two determinations made on different days of the same week one agreed closely with the position given on the diagram, and the other was almost twice as far out from the corner of the triangle. As the observations were made with the greatest of care and under exactly the same conditions on each occasion, and similar differences had been noticed on former occasions, there seems no doubt that the color-vision changes appreciably from day to day."

G. F. S.

**Application of an Optical Manometer to the Measurement of the Viscosity of Gases.** J. E. P. WAGSTAFF. (*Phil. Mag.*, Jan., 1923.)—A thin slip of glass of known modulus of elasticity forms the upper wall of a pressure chamber. Upon it rests a plate of glass one millimetre thick. The film of air between the slip and the plate is illuminated by a parallel beam of monochromatic light. The circular fringes there formed are viewed by a microscope. Any bulging of the thin slip will cause a radial motion of the fringes. The pressure chamber is connected to a partially exhausted reservoir, into which air may slowly flow from the outside atmosphere through a capillary tube. As the air enters, the pressure within both reservoir and pressure chamber rises and the glass slip bulges upward, causing the fringes to migrate in toward the centre. In one instance it took 43 seconds for 10 fringes to disappear, the pressure meanwhile rising through 18.1 cm. of mercury. There is, of course, a relation between the dimensions of the apparatus, the elastic coefficient of the glass slip and the viscosity. This last quantity was calculated from the data of the experiment to be  $1.811 \times 10^{-4}$  dynes per sq. cm. per unit velocity gradient.

G. F. S.



# THE FRANKLIN INSTITUTE.

---

*(Proceedings of the Stated Meeting held Wednesday, March 21, 1923.)*

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, March 21, 1923.

MR. W. C. L. EGLIN, Vice-president, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of:

Christo Casacof, Esq., Mechanical Engineer, 104 West 79th Street, New York City, New York.

Henry Walter Cockerill, Esq., Technical Clerk, 19 Rata Road, Hataitai, Wellington, New Zealand.

Antonius de Graaff, Esq., Chemical Engineer, Philips' Glowlampworks, Eindhoven, Holland.

John F. Metten, Esq., Chief Engineer, William Cramp and Sons Ship and Engine Building Company, Richmond and Norris Streets, Philadelphia, Pennsylvania.

Allen I. Myers, Esq., A.B., Instructor in Chemistry, Swarthmore College, Swarthmore, Pennsylvania.

Charles C. Roberts, Esq., Chemist, 75 W. Lacrosse Avenue, Lansdowne, Pennsylvania;

lectures before the Sections as follows:

"The Structure and Constitution of Alloys" by

Walter Rosenhain, D.Sc., F.R.S.,

Superintendent, Metallurgy Department,

National Physical Laboratory,

Teddington, England;

"High Temperature Investigation" by

Edwin F. Northrup, Ph.D.,

Princeton,

New Jersey;

"Ionization and Resonance Phenomena" by

Charles B. Bazzoni, Ph.D.,

Professor of Experimental Physics,

University of Pennsylvania,

Philadelphia, Pennsylvania;

and a lecture before the Stated Meeting, February 21, 1923, by

Clement E. Chase, C.E.

Principal Assistant Engineer

and

M. B. Case, B.Sc.,

Senior Resident Engineer,

Delaware River Bridge Joint Commission,

Philadelphia, Pennsylvania,



on "The Main Piers of the Bridge over the Delaware River between Philadelphia and Camden;"

also the following additions to the library: 38 bound volumes, 8 unbound volumes, 115 pamphlets and 7 photographs.

The Board of Managers also transmitted the following resolutions:

*Resolved*, That the Board of Managers of The Franklin Institute recommend to the Institute the election to Honorary Membership of Professor A. A. Michelson, Professor of Physics, the University of Chicago, Chicago, Illinois, who on the third of January was awarded the Institute's Franklin Medal "in recognition of his contributions of fundamental importance in physical science, especially his brilliant discoveries in the field of optics and astro-physics."

*Resolved*, That the Board of Managers of The Franklin Institute recommend to the Institute the election to Honorary Membership of General G. A. Ferrié, Chief Signal Officer of the French Army, Member of the French Academy, who on the third of January was awarded the Institute's Franklin Medal "in recognition of his long-continued and successful researches in the field of radio-transmission of intelligence and their splendid and successful military applications, and his eminent success in the organization and directing of the communication service of the French Army during the war."

On motion duly seconded, the report was accepted and the recommendations to elect to Honorary Membership Dr. A. A. Michelson, of Chicago, and General G. A. Ferrié, of Paris, France, were unanimously adopted.

The paper of the evening was presented by Dr. Harvey C. Hayes, Research Physicist, U. S. Navy, on "Measuring Ocean Depths by Acoustical Methods." The measurement of distances by acoustical methods and in particular with the measurement of submarine distances and the determination of submarine contours were first considered. The history of the subject was briefly outlined and the various devices that have been developed in connection with the problem were described. The research work carried out by the Navy Department during the past five years which has resulted in solving the problem of measuring submarine distances through the development of the "Sonic Depth Finder" were reviewed. Contour charts of the sea-bottom to depths exceeding three thousand fathoms were shown and certain possible interesting and valuable applications of the depth finder were pointed out. The subject was illustrated by lantern slides.

After a discussion, a unanimous vote of thanks was extended to the speaker. Adjourned.

R. B. OWENS,  
Secretary.



## COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday, March 7, 1923.)*

HALL OF THE INSTITUTE,  
PHILADELPHIA, March 7, 1923.

MR. W. H. FULWEILER *in the Chair*.

The following reports were presented for final action:

No. 2763: Universal Measuring Machine. The Edward Longstreth Medal to The Geneva Society of Geneva, Switzerland.

No. 2806: Literature. The Howard N. Potts Medal to Dr. Albert W. Hull, General Electric Company, Schenectady, New York, for his paper on "The Crystal Structure of the Common Elements," printed in the issue of the JOURNAL OF THE FRANKLIN INSTITUTE for February, 1922.

The following report was presented for first reading:

No. 2794: Smoot Regulating System.

R. B. OWENS,  
*Secretary*.

---

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, March 14, 1923.)*

#### RESIDENT MEMBERS.

MR. JOHN F. METTEN, Richmond and Norris Streets, Philadelphia, Pennsylvania.

MR. ALLEN I. MYERS, Swarthmore College, Swarthmore, Pennsylvania.

MR. CHARLES C. ROBERTS, 75 West Lacrosse Avenue, Lansdowne, Pennsylvania.

#### NON-RESIDENT.

MR. CHRISTO CASACOF, 104 West 79th Street, New York City, New York.

MR. H. W. COCKERILL, 19 Rata Road, Hataitai, Wellington, New Zealand.

MR. ANTONIUS DE GRAAFF, Philips' Glowlampworks, Eindhoven, Holland.

#### CHANGES OF ADDRESS.

MR. L. J. R. HOLST, Harvard Road, Brookline, Delaware County, Pennsylvania.

MR. A. DW. SMITH, 1732 Commercial Trust Building, Philadelphia, Pennsylvania.

MR. SAMUEL SPITZ, 2244 North Vanpelt Street, Philadelphia, Pennsylvania.

---

## NECROLOGY.

Mr. Calvin Pardee, 447 Drexel Building, Philadelphia, Pennsylvania.



## PUBLICATIONS RECEIVED.

*Die Luftstickstoffindustrie mit besonderer Berücksichtigung der Gewinnung von Ammoniak und Salpetersäure*, von Dr. Ing. Bruno Waeser. 586 pages, illustrations, 8vo. Leipzig, Otto Spamer, 1922. Price, in paper, 13.440 Marks.

*Elements de Mécanique à l'Usage des Ingenieurs*. Statique cinématique par Robert d'Adhémar. 254 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 16 Francs.

*Index Generalis*. General Year Book of the Universities, High Schools, Academies, Archives, Libraries, Scientific Institutions, Botanical and Zoological Gardens, Museums, Observatories and learned societies, published under the direction of R. de Montessus de Ballore. 2111 pages, 12mo. Paris, Gauthier-Villars et Cie., 1922-23. Price, in paper, 50 Francs.

*Ultra-violet Radiation—Its Properties, Production, Measurement, and Applications*, by M. Lukiesh, Director of Applied Science, Nela Research Laboratories. 258 pages, illustrations, plates, 8vo. New York, D. Van Nostrand Company, 1922.

*Théorie Mathématique des phénomènes Thermiques Produits par la Radiation Solaire*, par M. Milankovitch. 338 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1920. Price, 20 Francs.

*Cours de Chimie Inorganique*, par Fred. Swarts. Third edition, revised and enlarged, 734 pages, illustrations, 8vo. Bruxelles, Maurice Lamertin, 1922. Price, in paper, 50 Francs.

*Cours de Chimie Organique*, par Fred. Swarts. Third edition, revised and enlarged, 674 pages, illustrations, 8vo. Bruxelles, Maurice Lamertin, 1921. Price, in paper, 50 Francs.

*La Théorie de la Relativité d'Einstein et ses Bases Physiques*. Exposé élémentaire par Max Born. Traduit de l'allemand d'après la seconde édition par F. A. Finkelstein et J. G. Verdier. 339 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 25 Francs.

*La Théorie de l'Allotropie*, par A. Smits. Première édition française traduite par J. Gillis. 523 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 55 Francs.

*Gluc and Gelatin*, by Jerome Alexander. 236 pages, plate, 8vo. New York, Chemical Catalog Company, 1923. Price, \$3.

*Our Solar System and the Stellar Universe*. Ten popular lectures by Rev. Charles Whyte. 234 pages, plates, 8vo. London, Charles Griffin and Company, Ltd., Philadelphia, J. B. Lippincott Company, 1923.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

---

Vol. 195

MAY, 1923

No. 5

---

## THE ELECTRON IN CHEMISTRY.\*

BY

SIR JOSEPH JOHN THOMSON, O.M., F.R.S., LL.D., Ph.D., D.Sc.

Master of Trinity College, Cambridge, England,  
Franklin Medallist, Honorary Member of the Institute.

I OUGHT to explain why it is that I, who am a physicist and not a chemist, have chosen chemistry as the subject of these lectures. I have done so because I believe that the introduction of the idea of the electron will break down, and indeed has already done so to some extent, the barrier of ignorance which has divided the study of the properties of matter into two distinct sciences, physics and chemistry. The properties of matter which are of primary importance to the chemist are those which relate to the power of atoms to unite together to form new combinations, new compounds. The ability to do this and the type of compound formed vary enormously from one chemical element to another. Until recently the conception formed by the physicist of the atom afforded no clue to this variation in the chemical properties of the atom and gave therefore but little guidance to the chemist in what he regarded, and quite rightly, as the most important part of his work. The chemist wants to know much more about the difference between an atom of hydrogen and one of oxygen than that the atom of hydrogen is a small particle of one kind of matter and

---

\* A series of lectures given before The Franklin Institute, April 9-13, 1923, see page 724.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.

VOL. 195, No. 1169—41

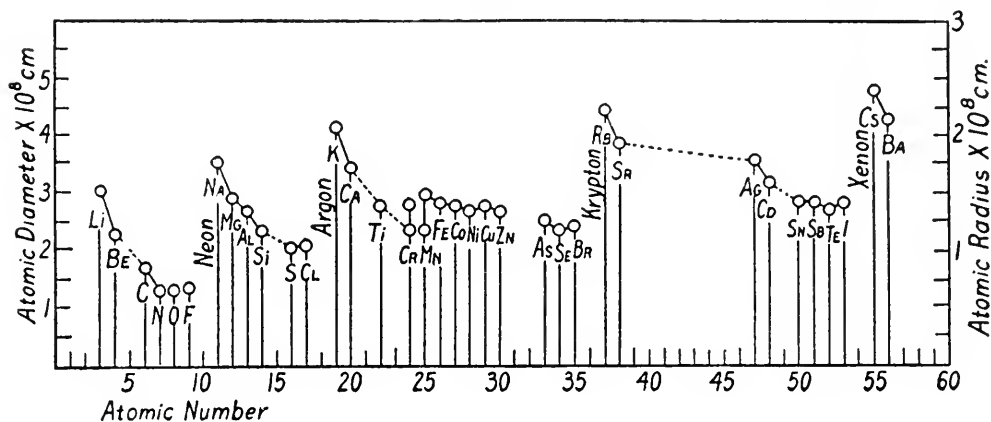
593



the atom of oxygen a heavier particle of another kind of matter. This lack of knowledge led to a proposal made by a distinguished chemist at the beginning of this century to give up the atomic theory and base chemistry on statistical and thermodynamical considerations.

The chemist wants to know the reason why the behaviour of an atom of hydrogen is so different from that of one of oxygen. This must depend upon the differences in the constitution of the two atoms themselves. Thus to explain the difference between the chemical properties of different atoms we have to go a stage further than the atomic theory. Just as some of the physical

FIG. I.



properties of matter in bulk had required for their explanation the conception that matter is not continuous but has a structure of finite and measurable fineness, so no progress could be made towards the explanation of their chemical properties until we gave up the idea that the atom was indivisible, continuous and uniform, and assigned to atoms as well as to solids and liquids a structure of their own. The discovery of the electron in 1897 was the first direct evidence of such a structure. It was shown that these electrons came from all types of atoms, and that whatever the source there was only one kind of electron, which has a mass only about  $1/1700$  that of an atom of hydrogen and carries a charge of negative electricity numerically equal to the positive charge associated with an atom of hydrogen in the electrolysis of solutions.

Thus an invariable electron was proved to be a constituent of all atoms. Means were then devised to measure the number of electrons in the atoms of the different chemical elements. It



was found that this number was finite and varied from element to element, and that the number of electrons in the atom of an element was equal to the atomic number of the element: The atomic number of an element being its place in the list when the elements are arranged in the order of their atomic weights. As the atomic number is roughly proportional to the atomic weight the proportion between the mass of the electron and the total mass of an atom is, except for hydrogen, much the same for all atoms. The electrons, however, only account for about  $1/3400$  of the whole mass, for most purposes a negligible fraction.

The greater part of the mass is accounted for by the positively electrified part of the atom. The electrons are all negatively electrified and as the normal atom is electrically neutral, there must be within it a positive charge to balance the negative one on the electrons. This positive charge, as experiments on positive rays show, is attached to a mass equal to the mass of the atom. Thus the carrier of the positive charge, unlike that of the negative, varies from element to element. As the mass of the positive charge is always an integral multiple of a unit, it is natural to suppose that this mass is made up of a number of units bound together. The number of such units is equal to the atomic weight and the number of electrons approximately half that number, if each unit of mass carries the atomic charge of positive electricity, the quantity of positive electricity would be too large unless these positive units were associated with about half this number of electrons. Thus, in addition to the structure conferred by the electrons, the positively electrified parts have themselves a structure, it is the structure conferred by the electrons which is responsible for the chemical properties of the atom, the structure of the positive core is concerned with radioactive transformations.

As up to the present nothing has been discovered that cannot be resolved into electrons and positively electrified particles, it is natural to frame a theory of the structure of the atom on the supposition that it is built up of these two ingredients. It should be borne in mind, however, that our means of detecting the existence of electrically charged bodies far surpass those for detecting uncharged ones, and if there were any uncharged constituents of the atom, they would in any case probably have escaped detection. We know, however, even supposing that such constituents do exist, their mass must be negligible compared with that of the positive



parts, for these parts account for well within a fraction of a per cent. of the whole mass of the atom.

#### ARRANGEMENT OF ELECTRONS IN THE ATOM.

Confining ourselves then to the consideration of things whose existence has been demonstrated we regard the atom as made up of a massive positively electrified centre surrounded by electrons. The number of electrons increasing from one in the atom of hydrogen to a hundred or more in the heavier elements. The positive charge of the centre and the negative charges on the electrons will produce a field of electrical force which will be determinable when the position of the electrons can be specified. Thus the force exerted by the atom and therefore its chemical properties will depend upon the configuration of the electrons and to determine this is one of the most important problems in the electron theory of chemistry.

This problem is that of determining the way the electrons will arrange themselves under the action of their mutual repulsions and the forces exerted upon them by the positive charge.

In the first place we observe that if these forces were to vary strictly as the inverse square of the distance we know by Earnshaw's theorem that no stable configuration in which the electrons are at rest or oscillating about positions of equilibrium is possible, the electrons must describe orbits, and further they must describe different orbits; for such a system as that in Saturn's rings where several units follow each other round the same orbit is not possible when the units, as the electrons would do, repel each other instead of attracting one another like the constituents of Saturn's rings. When there are several electrons in the atom the orbits described by the electrons would be of great complexity, and the mental picture conveyed by this multitude of orbits would be too blurred and complicated to be of much assistance in helping us to get readily a clear idea of what is going on in chemical processes.

I have therefore adopted the plan of supposing that the law of force between the positive part and the electrons is, at the distances with which we have to deal in the atom, not strictly that of the inverse square, but a more complex one which changes from attraction to repulsion as the distance between the positive charge and the electron diminishes. This hypothesis leads to a simple mental picture of the structure of the atom and its conse-



quences are in close agreement with the facts of chemistry. I suppose that the repulsive force between two *electrons* is always inversely proportional to the square of the distance. With regard to this point I may point out that we have no direct evidence as to what may be the law of force between electrical charges at distances comparable to  $10^{-8}$  cm., which is a distance which we have reason to believe is comparable with that which separates the positive charge from the electron in the atom. The direct experimental verification of this law has been of course made at incomparably greater distances, while the direct experiments, such as those on the scattering of the alpha particles, only give information as to the law at distances very small compared with  $10^{-8}$  cm.

I shall assume that the law of force between a positive charge and an electron is expressed by the equation

$$F = \frac{Ee}{r^2} \left( 1 - \frac{c}{r} \right) \quad (1)$$

where  $F$  is the attraction between the charges,  $E$ ,  $e$ , the positive and negative charges on the core and electrons, respectively,  $r$  the distance between them and  $c$  is a constant varying from one kind of atom to another, it is the distance at which the force changes from attraction to repulsion and is of the order of  $10^{-8}$  cm.

We may remark in passing that the introduction of some new physical law, involving directly or indirectly a length of this order, is necessary for any theory of the structure of atoms. We could not form a theory at all if all we knew about the action of electric charges was that they repelled or attracted inversely as the square of the distance, for this would put at our disposal only two quantities, the mass of an electron and its charge, and so could not furnish the three units of space, mass and time required for any physical theory. The discovery of the induction of currents or what is equivalent, the magnetic effect due to electric charges, introduced another fundamental unit the velocity of light; the unit of length to which this system leads is the radius of the electron, about  $10^{-13}$  cm., a quantity of quite different order from  $10^{-8}$  cm., which corresponds to atomic dimensions. The size of atoms being what it is, is a proof that there is some law of physics not recognized in the older science which is all-important in connection with the theory of the atom and must form the basis of that theory.



If the law of force is that just given, then a number of electrons can be in stable equilibrium around a positive charge without necessarily describing orbits around it.

#### ONE ELECTRON ATOM.

Thus, for example, if there is one electron it will be in stable equilibrium at a distance  $c_1$  from the positive charge.

#### TWO ELECTRON ATOM.

If there are two electrons they will be in equilibrium with the positive charge midway between them,  $r$  the distance of either electron from the positive charge is given by the equation

$$\frac{Ee}{r^2} \left( 1 - \frac{c_2}{r} \right) = \frac{c^2}{4r^2} \quad (2)$$

When the positive charge and the two electrons form an electrically neutral system  $E = 2e$ , so that  $c_2/r = 7/8$  or  $r = 1.14 c_2$ .

#### THREE ELECTRON ATOM.

When there are three electrons, they will be in equilibrium at the corner of an equilateral triangle with the positive charge at the centre.  $r$ , the distance of any electron from the centre, is given by the equation

$$\frac{Ee}{r^2} \left( 1 - \frac{c_3}{r} \right) = \frac{2}{3r^2} \cos 30 \quad (3)$$

When the system is electrically neutral  $E = 3e$ , so that  $r = 1.26 c_3$ .

#### FOUR ELECTRON ATOM.

The most symmetrical arrangement of four electrons is when they are at the corners of a regular tetrahedron. The distance of the electrons from the centre when the atom is neutral is equal to  $1.29 c_4$ . The tetrahedron may be regarded as the ends of two equal lines at right angles to each other and also to the line joining their middle points.

#### FIVE ELECTRON ATOM.

Five electrons are in equilibrium when arranged so that three are at the corners of an equilateral triangle, the other two at the ends of a line passing through the centre of the triangle and at



right angles to its plane; the line is bisected by the plane of the triangle. The distance of the electrons in the triangle from the centre is  $1.34 c_5$ , that of the other two  $1.37 c_5$ .

#### SIX ELECTRON ATOM.

Six electrons are in equilibrium when at the corners of a regular octahedron. For some purposes it is convenient to regard the octahedron as two equilateral triangles at right angles to the line joining their centres, one triangle being twisted relatively to the other so that the projection of their corners on a parallel plane forms a regular hexagon. The distance of the electrons from the centre is  $1.38 c_6$ .

#### SEVEN ELECTRON ATOM.

Seven electrons arrange themselves so that five are at the corners of a regular pentagon while the two others are at the ends of a line through the centre at right angles to the plane of the pentagon and which is bisected by that plane. The distance of the electrons in the pentagon from the centre is  $1.4 c_7$ , that of the other two  $1.37 c_7$ .

#### EIGHT ELECTRON ATOM.

Eight electrons arrange themselves at the corners of a twisted cube, a figure obtained by taking two squares, placing them parallel to each other and at right angles to the line joining their centres, and twisting them relatively to each other so that the projection of their corners on a parallel plane forms a regular octagon.

#### CONFIGURATION WHEN THE NUMBER OF ELECTRONS IS GREATER THAN EIGHT.

The following considerations show, however, that there must come a stage when it will no longer be possible to have all the electrons at the corners of a regular polyhedron.

To keep the electrons in stable equilibrium in spite of their mutual repulsion requires a finite positive charge and the greater the number of electrons and therefore the smaller the angular distance between an electron and its nearest neighbour, the greater the positive charge must be.

In Table I, I give the results of a calculation of the positive charge  $E$  required to keep  $n$  electrons in stable equilibrium.



The first line refers to the two-dimensional problem, when the electrons are arranged at equal intervals round the circumference of a circle with a positive charge at the centre; the second line refers to the three-dimensional problem when the electrons are at the corners of a polyhedron.

These numbers are for a law of force between the positive charge and the electron represented by  $\frac{Ee}{r^2} \left( 1 - \frac{c}{r} \right)$ . If the part of the force which does not vary inversely as the square of the distance varies inversely as some higher power than the cube, then the number of electrons which a given positive charge can keep in stable equilibrium will be increased.

TABLE I.

<i>Two-dimensional problem.</i>											
$n = 1$	2	3	4	5	6	7	10	12	14	16	8
$E/e > 0$	.75	1.58	3.10	4.76	7.32	14.2	24.48	38.9	58	83	115

<i>Three-dimensional problem.</i>							
$n = 1$	2	3	4	6	8	12	20
$E/e > 0$	.75	1.58	2.44	4.8	7.6	13	30

Confining ourselves for the moment to the case when the force is represented by  $F = \frac{Ee}{r^2} \left( 1 - \frac{c}{r} \right)$ , we see from the second table that when the number of electrons is not greater than eight, the electrons can be kept in equilibrium by a positive charge equal to the sum of the negative charges on the electrons, which is the greatest positive charge which can occur in a neutral atom. So that when the number of electrons is not greater than eight, a neutral atom can have these electrons arranged symmetrically at the same distance from the centre at the corners of a regular polyhedron. When, however, the number exceeds eight this is no longer possible. For we see from the table that to keep, say, nine electrons in stable equilibrium would require a positive charge more than  $9e$ , where  $e$  is the charge on an electron, but in a neutral molecule  $9e$  is the maximum positive charge available when there are nine electrons in the atom. Thus the regular progression in the arrangement breaks down when the electrons amount to eight and a new arrangement must come into force.



Let us suppose that there are nine electrons; then these nine cannot all be arranged at the same distance from the centre, for this arrangement would be unstable since a positive charge of nine is insufficient to keep nine electrons in stable equilibrium. The charge  $9e$  could, however, keep eight electrons in stable equilibrium at the same distance from the centre, leaving one to go outside. The distance of the eight electrons from the central charge would be  $1.38 c_9$ , that of the single electron would be  $9 c_9$ . So that the single electron would be a long way out from the centre of the atom.

If there are ten electrons, these can be arranged so that eight form a layer round the centre and two go outside, the distance of the eight from the centre would be  $1.33 c_{10}$ , that of the two outlying ones would be  $5.7 c_{10}$ .

Eleven electrons can be arranged with an inner layer of eight and an outer one of three, the distance of the inner one from the centre would be  $1.3 c_{11}$ , that of the outer one  $4.625 c_{11}$ .

Twelve electrons might be arranged with an inner layer of eight, radius  $1.26 c_{12}$  and an outer layer of four, radius  $3.9 c_{12}$ .

Thirteen electrons, with an inner layer of eight, radius  $1.227 c_{13}$  and an outer layer of five, mean radius  $3.52 c_{13}$ .

Fourteen electrons, with an inner layer of eight, radius  $1.22 c_{14}$ ; and an outer layer of six, radius  $3.22 c_{14}$ .

Fifteen electrons, with an inner layer of eight, radius  $1.2 c_{15}$ ; an outer layer of seven, mean radius  $3.1 c_{15}$ .

Sixteen electrons, with an inner layer of eight, radius  $1.18 c_{16}$ ; an outer layer of eight, radius  $2.9 c_{16}$ .

We have now got eight electrons on the outer layer and there is not accommodation for any more; for since the atom is neutral the excess of positive over negative electricity in the system consisting of the central charge and the inner layer is equal to the charge on the electrons in the outer layer, thus if there were nine electrons in the outer layer there would be only an effective positive charge of nine to keep them in equilibrium. We can, however, get a system which will be in stable equilibrium if the electrons proceed to form a third shell; thus, if there are seventeen electrons, we could have an inner shell of eight, then another shell of eight and then an electron a long way outside. If we had eighteen electrons we should get two shells of eight and two electrons out-



side, and so on, until with twenty-four electrons we shall have filled up the third shell and have to begin again.

Let us now arrange the lighter elements in the order of the number of electrons they contain, and place underneath the symbol for the element the number of electrons in the outer layer of the atom. The number of free electrons in the atom has been taken as two less than the atomic number of the element, since two electrons always seem to cluster round the centre core and form a system by themselves.

TABLE II.

	Li	Be	Bo	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	A	K
Number of free electrons in the atom . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Number of electrons in the outer layer .	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1

#### THE PERIODIC LAW.

Thus, if we arrange the elements in the order of the number of electrons in the atom, which we have seen is the same as the order of the atomic weights, there will be a periodicity in the number of electrons in the outer layer. It will increase from one to eight, then drop again to one; increase again to eight, drop to one, and so on. Thus, as far as properties depending upon the outer layer are concerned, the elements will show a periodicity in their properties similar to that expressed by Mendeleef's periodic law in chemistry.

We shall show later on that the valency is a property depending on the number of electrons in the outer layer, the electropositive valency being proportional to that number, so that this type of atom would explain the periodic law.

#### VARIATION OF THE NUMBER OF ELEMENTS IN A PERIOD.

We have supposed that when the positive charge and therefore the number of electrons in the atom is increased by unity, the additional electron goes to the outer layer. This need not, however, necessarily be the case. When the positive charge is in-



creased, the number of electrons which it can hold in stable equilibrium on a spherical layer with its centre at the atom increases also; thus a large positive charge at the centre could hold more than eight electrons in the inner layer, and so the additional electron might, instead of going to the outside, find accommodation on one of the inner layers. Thus, since the valency depends on the number of electrons in the outer layer, if the additional electron was trapped in an inner layer, two consecutive elements, though they would have different atomic weights, would have the same valency. When there are a large number of electrons in the atom arranged in many layers it may require the addition of several electrons to the atom before there is any increase in the number in the outer layer and thus there might be a considerable number of adjacent elements with different atomic weights but with very similar chemical properties. There are groups of elements such as the iron, nickel and cobalt group, the rhodium group, the crowd of elements known as the rare earths, and the platinum group which fulfil this condition.

#### ALLOTROPIC FORMS.

There is in general more than one way in which the electrons can be arranged in stable equilibrium and though one particular arrangement may have the absolute minimum potential energy, yet calculation shows that in some cases the difference in potential energy between this configuration and some other one is exceedingly small and changes in the surroundings change the balance in favour of one or the other. If these configurations have different numbers of electrons in the outer layer, then they would correspond to forms with different valencies, and thus we may look in this direction for an explanation of the variable valencies shown by some elements. We shall return to this point later on.

The following table, calculated by Miss Woodward, gives in the third column the potential energy corresponding to the various arrangements of the electrons in atoms containing from three to eight electrons. The second column contains the distances of the electrons from the centre of the atom. Thus the figures corresponding to the arrangement of seven electrons in a double triangular pyramid with two electrons outside on the axis of the pyramid, indicate that the electrons on the triangular base are at a distance  $1.244 c$  from the centre: those at the vortex of the inner



TABLE III.

*Potential Energy of Atoms with Three to Eight Electrons.*

Arrangement of Electrons.	Distances of Electrons from Atom.	Potential Energy.
<i>Eight electrons.</i>		
(i) One layer—twisted cube	1.447 $c$	$-16.75 \ e^2/c$
(ii) One layer—cube	1.446 $c$	$-15.28 \ e^2/c$
(iii) Two layers—tetrahedra similarly orientated	$\left\{ \begin{array}{l} 1.105 \ c \ (4) \\ 3.108 \ c \ (4) \end{array} \right.$	$\left. \right\} -14.77 \ e^2/c$
(iv) Two layers—six electrons in inner, two in outer ring	$\left\{ \begin{array}{l} 1.282 \ c \ (4) \\ 1.267 \ c \ (2) \\ 4.80 \ c \ (2) \end{array} \right.$	$\left. \right\} -15.012 \ e^2/c$
<i>Seven electrons.</i>		
(i) One layer	$\left\{ \begin{array}{l} 1.37 \ c \ (2) \\ 1.439 \ c \ (5) \end{array} \right.$	$\left. \right\} -12.181 \ e^2/c$
(ii) Two layers—five in inner, two in outer ring	$\left\{ \begin{array}{l} 1.244 \ c \ (3) \\ 1.191 \ c \ (2) \\ 4.316 \ c \ (2) \end{array} \right.$	$\left. \right\} -12.096 \ e^2/c$
<i>Six electrons.</i>		
(i) One layer	1.385 $c$	$-9.40 \ e^2/c$
(ii) Two layers—four in inner, two in outer ring	$\left\{ \begin{array}{l} 1.196 \ c \ (4) \\ 3.55 \ c \ (2) \end{array} \right.$	$\left. \right\} -8.868 \ e^2/c$
<i>Five electrons.</i>		
(i) One layer	$\left\{ \begin{array}{l} 1.342 \ c \ (3) \\ 1.376 \ c \ (2) \end{array} \right.$	$\left. \right\} -6.806 \ e^2/c$
(ii) Two layers—four in inner, one in outer ring	$\left\{ \begin{array}{l} 1.273 \ c \ (3) \\ 1.134 \ c \ (1) \\ 5.105 \ c \ (1) \end{array} \right.$	$\left. \right\} -6.667 \ e^2/c$
<i>Four electrons.</i>		
(i) One layer—corners of square	1.298 $c$	$-4.748 \ e^2/c$
<i>Three electrons.</i>		
(i) One layer—equilateral triangle	1.238 $c$	$-2.934 \ e^2/c$
(ii) Electrons on a straight line through atom	$\left\{ \begin{array}{l} 1.087 \ c \\ 1.035 \ c \\ 3.577 \ c \end{array} \right.$	$\left. \right\} -2.787 \ e^2/c$



pyramid at the distance 1.191  $c$  while the outer electrons are at a distance 4.316  $c$ .

A simple example of the small difference in the potential energy between different configurations is afforded by an atom containing five electrons. We have described one such configuration when the five electrons were approximately at the same distance from the centre. There is, however, as we see from the table, another arrangement where four electrons are at the corners of a regular tetrahedron with its centre at the positive charge, while the fifth electron is a long way outside the tetrahedron. The mean distance of the electrons on the tetrahedron from the centre is approximately 1.22  $c_5$ ; where  $c_5$  is the value of  $c$  for the fifth electron atom, while that of the outside electron is approximately 5  $c_5$ , *i.e.*, more than four times greater. The potential energy of the second configuration is only about two per cent. greater than the first, thus there would be no great tendency for the second configuration to pass back to the other. The properties of the two configurations would, however, be quite different, in the second configuration we have a single electron far away from the others, this, as we have seen, is also the case with the alkali metals, in this configuration the five electron atom might be expected to show some of the properties of a monovalent element, in the other it would be pentavalent.

#### ACTIVE NITROGEN.

As nitrogen has an atom with five disposable electrons, it seems possible that the active form of nitrogen discovered by the present Lord Rayleigh may have this configuration. This active form is produced by passing an electric discharge through nitrogen and it is clear that if an atom were first ionised by the detachment of an electron the conditions would be favourable for the production of the configuration under consideration. For when the first electron is detached the remaining four will naturally arrange themselves in a tetrahedron round the centre, thus the nucleus of the configuration is already there and an additional electron at some distance from the centre would be more likely to take up a position outside than to force itself into the tetrahedron. As the second form has, like the alkali metals, a single electron at a great distance from the centre, we should expect that like them it would be attacked vigorously by halogens, and that as the outlying elec-



tron would require little work to detach it, this form of nitrogen would be easily ionised; both these properties are characteristic of Lord Rayleigh's active nitrogen.

We see that besides the two forms for the fifth electron atom there are forms for the sixth and seventh electron atoms which differ little in their potential energy in which two electrons are separated from the rest (*e.g.*, oxygen and fluorine). These would tend to be formed if the atoms were ionised so as to lose two electrons and then regain these electrons. As the number of atoms which lose two electrons when the electric discharge passes through a gas is small compared with the number which only lose one, we should not expect these modifications of oxygen and fluorine to be produced so freely as those of nitrogen.

#### EXPERIMENTAL EVIDENCE AS TO THE CONFIGURATION OF ELECTRONS IN THE ATOM.

We may hope when our sources of Röntgen radiation are more powerful to be able to obtain evidence of this by observing the interference effects produced when Röntgen rays pass through large numbers of neutral atoms. If the orientation of these atoms is a random one we can easily show that the interference of the rays scattered by the electrons will give rise to a series of rings. There will be a separate ring for every different distance between pairs of electrons in the atom. Thus if there were only two electrons there would only be one ring whose radius is proportional to the distance between the two electrons; again in an equilateral triangle there would only be one ring, for the distance between any two electrons is equal to a side of the triangle. If four electrons were at the corners of a regular tetrahedron there would again be only one ring for the distance between any two electrons is equal to a side of the tetrahedron. If, however, the four electrons were at the corners of a square there would be two rings, the radius of one being proportional to a side of the square, that of the other to its diagonal. Arrangement at the corners of a regular octahedron would also give two rings, the radius of one being proportional to the side of the octahedron, the other to the distance between two opposite corners. A cubical arrangement of electrons would, however, give three rings, the radius of one proportional to a side of the cube, that of the second to a diagonal



of a face and that of the third to the diagonal of the cube. Evidence of this kind is not, however, available at present.

As we shall see later on, the coefficient of diamagnetism gives on Langevin's theory of diamagnetism, the moment of inertia of the electrons about a line through the centre of the atom, this can be made to yield a certain amount of information about the disposition of the electrons, especially if we know from other sources the distance of the outer layer of electrons from the centre of the atom.

#### EVIDENCE AFFORDED BY POSITIVE RAYS.

More definite information can be got from evidence afforded by the positive rays. Let us first take the case of positively charged atoms. Their positive charge is due to their having lost electrons from the outer layer, now on this theory there is only one electron in the outer layer of the atom of hydrogen and in those of the alkali metals, so that these atoms should not be able to lose more than one electron and therefore should be unable to gain more than one unit of positive charge.

It is remarkable that these are the only atoms which in the positive ray spectra have not been observed with more than one positive charge. On the other hand, other light atoms have more than one electron and thus gain double or treble positive charges.

All such atoms when detected in the positive ray spectrum have been observed with double positive charges and in some cases such as carbon, nitrogen, oxygen with three or four, while as many as seven positive charges have been found in the atom of mercury.

Further confirmation of the views we have been discussing about the relation between the number of electrons and the property of the atom is afforded by the study of the occurrence of negatively electrified atoms in a gas through which an electric discharge is passing. By the method of the positive rays we are able to detect negatively as well as positively electrified atoms, and we find in this way that some atoms readily acquire a negative charge while others never do so. On the view we are considering, eight is the maximum number of electrons which can exist in the outer layer; as the atom of neon already possesses this number it cannot accommodate another electron and so cannot receive a negative charge. On the other hand the atom with a smaller



number of electrons in the outer layer has, as a reference to Table II shows, a superfluity of stability and can therefore accommodate another electron and thus acquire a negative charge. The superfluidity of stability is not, however, great enough for them to accommodate two electrons so that we should not expect to find any atoms with a double negative charge.

In the experiments with positive rays the atom of neon which has eight electrons in the outer layer has never been observed with a negative charge, while negative charges are common on atoms of hydrogen, chlorine, carbon and oxygen. No atoms have been observed carrying two negative charges.

It is remarkable that though carbon and oxygen, the neighbours on either side of nitrogen, readily acquire negative charges, nitrogen itself is very rarely observed with a negative charge. It was thought for a long time that the nitrogen atom never carried a negative charge, recently, however, I have observed in more intense discharges a faint line on the positive ray photograph corresponding to the negatively charged nitrogen atom, it is, however, very feeble in comparison with the adjacent lines due to negatively charged carbon and oxygen, respectively. A calculation of the work required to remove the additional electron from a negatively charged nitrogen atom shows that it is very small in comparison with that required to remove the additional electrons from negatively charged atoms of carbon or oxygen, so that a negatively charged nitrogen atom would easily lose its charge and so be difficult to detect.

Again the only negatively electrified atoms we can observe by the positive ray method are those which have previously been positively charged, *i.e.*, those which at one time have lost an electron. If such atoms, when they regain electrons, are in the condition we have ascribed to "active nitrogen" the electrons they regain will be far out from the centre of the atom and so would be very easily detached. Thus very few of those atoms could be expected to retain the electrons necessary to give them a negative charge.

There are some other interesting results which follow at once from the view we have taken of the constitution of the atom. The first we shall consider is the change in the chemical properties produced by electrifying the atom. Let us take the oxygen atom as an example, it has six electrons in the outer layer, and we



may anticipate the results to be given in the next chapter by saying that its valency is determined by the number of electrons in this layer. When the oxygen atom is positively electrified it has lost one or more electrons. If it is electrified so that it carries one unit of positive charge, the unit of charge being that carried by an electron, it must have lost one electron, so that the atom will only have five electrons in the outer layer, the same number as there are in a neutral atom of nitrogen. Thus, if the valency depends on the number of electrons in the outer layer, the valency of oxygen carrying a unit charge of electricity ought to be the same as that of a neutral atom of nitrogen, *i.e.*, it ought to form the compound  $\text{OH}_3$ , a compound having the molecular weight 19. This is confirmed by observation with the positive rays, when hydrogen and oxygen are present in the tube, a line corresponding to this molecular weight is frequently observed. Again, if the oxygen atom carries a double positive charge, and observations on the positive rays show that oxygen atoms with this charge are frequent when the electric discharge passes through gases, the atom must have lost two electrons and will be left with only four in the outer layer, the same number as in the outer layer of a neutral atom of carbon; hence the doubly charged oxygen atom ought to have the same valency as neutral carbon, and thus form the compound  $(\text{OH}_4)^+ +$ . This compound would carry a double charge and the ratio of  $m/e$  would be 10. I have found<sup>1</sup> in the positive ray, spectrum lines having this value of  $e/m$  when both oxygen and hydrogen were in the discharge tube.

Again the atoms of the inert gases which have eight electrons in the outer layer, would, if they acquired one unit of positive charge, have lost an electron and would only contain seven electrons in the outer layer. This is the number in the outer layer of a neutral halogen atom. The positively electrified atoms of the inert gases could thus like the neutral atoms of the halogens combine with one atom of hydrogen and thus the compound  $\text{NeH}$  would be possible if it carried a unit charge of positive electricity.

The molecular weight of this would be 21 and a line corresponding to a carrier with this molecular weight has been observed by Aston. The neon atom can, as observations on the positive rays show, lose two electrons, in this state it could combine with two

---

<sup>1</sup> *Proc. Roy. Soc.*, 101, p. 290.



atoms of hydrogen, or one of oxygen, the first of these molecules would have the value  $m/e = 11$ , and the second  $m/e = 18$ ; the first could not be distinguished from the isotope of neon atomic weight 22 with a double charge, and the line due to the second would be identical with that due to water, so that the positive rays could not afford convincing evidence of the existence of these compounds. If we turn to negatively electrified atoms, a negatively electrified chlorine atom would have eight electrons in the outer layer, it would resemble the neutral atom of an inert gas and so would not be able to enter into chemical combination. It would seem as if it ought not to be very difficult to determine this point by direct experiment.

The negatively electrified chlorine atom has the same number of electrons as a neutral atom of argon, both having eight in the outer layer. It might therefore be expected to resemble argon not merely in its chemical properties, but also in the nature of its spectrum. The spectra would not be identical, for the positive charge binding the electrons together would be greater for argon than for chlorine. The similarity in the arrangement of the electrons might be expected to lead to similarities in the spectra of negatively electrified chlorine atoms and neutral argon atoms. Again, a positively electrified potassium atom has lost an electron and so would contain the same number of electrons as a negatively electrified chlorine atom or a neutral argon one. Thus we should expect the spectrum of positively electrified potassium atoms to show similarities both with that of negatively electrified chlorine atoms and with neutral argon atoms. Professor Zeeman and Mr. Dik<sup>2</sup> have compared the red spectrum of argon, which is the one due to the neutral atom, with the spectrum due to positively electrified potassium atom and have found some exceedingly interesting points of resemblance. It is easier to observe the spectra due to positively electrified atoms than those due to negatively electrified ones, for in the latter case we should have to observe the spectrum they give out on receiving the negative charge, any attempt to stimulate them to luminescence afterwards would probably result in their destruction.

Similarly positively electrified oxygen atoms might be expected to give spectra resembling those of neutral nitrogen atoms

---

<sup>2</sup> *Proc. Amsterdam Akademie*, 25, pt. 3 and 4.



and positively electrified nitrogen atoms show similarities with neutral carbon atoms.

#### THE SIZE OF ATOMS.

By the radius of an atom we mean the distance of the electron in the outer layer from the centre of the atom. Let  $E$  be the central positive charge and

$$\frac{Ee}{r^2} - \frac{e^2C}{r^3} \quad (4)$$

the attraction between this charge and an electron at a distance  $r$ ,  $e$  is the charge on the electron and  $eC = cE$  where  $c$  is the quantity introduced in the expression for the same force (formula (1)),  $c$  is the distance at which the force between the positive charge and the electron changes from attraction to repulsion.

Then for the equilibrium of an electron on the outer layer we have

$$\frac{Ee}{r^2} - \frac{Ce^2}{r^3} = \frac{S_n}{4r^2} e, \quad (5)$$

where  $S_n = \sum \frac{1}{\sin \theta}$ ,  $2\theta$  being the angle subtended at the centre of the atom by a pair of electrons and  $\sum \frac{1}{\sin \theta}$  means that the sum of the values of  $1/\sin \theta$  for each pair of electrons is to be taken. We get from this equation

$$r = \frac{C}{\frac{E}{e} - \frac{S_n}{4}} \quad (6)$$

The values of  $r$  for the lighter elements are given in the third column of Table IV. The fourth column is the value of  $r$  on the assumption that  $C$  is a linear function of the atomic weight, given by the equation  $C = aN + b$ , where  $N$  is the atomic weight and  $a$  and  $b$  constants.

Thus, taking the elements from lithium to neon, we see that the radius of the outer layer is greatest for the light elements and diminishes rapidly at first and then very slowly to the end of the period. When we pass from neon, the last element in this period, to sodium, the first in the next, there is a large increase in the radius. The sodium atom will have a larger radius than the lithium one, the ratio of the two will depend on the ratio of  $a$  to  $b$ , if  $a$  were zero the radii would be equal.



The increase in the radius which occurs at sodium is followed by a continually diminishing radius until we reach argon; when we pass to potassium, the first element in the next period, there is again an increase. The radii of atoms in the same group like lithium, sodium, potassium, or fluorine, bromine and iodine increase with the atomic weight of the element.

The relation between the radius of the atom and the atomic weight is such that the minima radii occur at the ends of the periods and, as in Lothar Meyer's well-known graph, which has been reproduced in almost every text-book of chemistry, not

TABLE IV.

Element.	N	$E/\epsilon$	$S_n$	$r$	
Hydrogen . . . . .	1	1	0	$C_H$	$a + b$
Lithium . . . . .	7	1	0	$C_{Li}$	$7a + b$
Beryllium . . . . .	9	2	1	$4C_{Be}/7$	$5.14a + .57b$
Boron . . . . .	11	3	2.3	$4C_{Bo}/9.7$	$4.52a + .412b$
Carbon . . . . .	12	4	3.66	$4C_C/12.3$	$3.88a + .322b$
Nitrogen . . . . .	14	5	5.2	$4C_N/14.8$	$3.78a + .270b$
Oxygen . . . . .	16	6	6.68	$4C_O/17.3$	$3.69a + .23b$
Fluorine . . . . .	19	7	8.08	$4C_F/19.9$	$3.8a + .21b$
Neon . . . . .	20	8	10.1	$4C_{Ne}/21.9$	$3.63a + .182$
Sodium . . . . .	23	1	0	$C_{Na}$	$23a + b$

at the middle. Recent experiments have shown, however, that this graph does not accurately represent the relation. Gervaise le Bas,<sup>3</sup> says,

1. "There is a periodic relation between the atomic volume and the atomic weight of the elements."

2. There is a tendency for the atomic volume to diminish in each series as the atoms increase in weight, the smallest occurs in group 7.

3. There is a general increase in the atomic volumes of each group from series one onwards, that is in the direction of increasing atomic weight.

This is in entire agreement with the results we have just found. The same thing is beautifully shown by the experiments

<sup>3</sup> "Molecular Volumes of Liquid Chemical Compounds," p. 237.



of W. L. Bragg<sup>4</sup> which give a curve (Fig. 1) for the atomic radii which in the period from lithium to neon agrees numerically very well with those deduced from the table (IV) given above, especially if  $b$  is small compared with  $a$ . The formula we have given would, unless  $a$  were very small compared with  $b$ , make the increase in atomic volume from lithium to sodium too great. According to Bragg the value of the sodium atom is only about 1.2 times that of the lithium one. While if the formula could be stretched from one period to another the increase would be much greater unless  $a$  were very small compared with  $b$ . We shall see later on that the law of the inverse cube only holds within a limited range of  $r$  and that beyond a certain distance the force seems to vary as the simple law of the inverse square. An effect of this kind would prevent any large increase in the radius of the atom as we passed from one period to another, and we should expect to find, as is the case, that the agreement between theory and experiment is most marked for the lighter and smaller atom.

#### IONISING POTENTIAL.

Another quantity which has been the subject of a great many experiments is what is known as the ionising potential. This is the work required to detach an electron from the atom, expressed as the fall of the charge on an electron through this potential. We may remark that the work required to detach the electron must depend upon the way in which it is done, so that the ionising potential is not a perfectly definite quantity. Thus to take two extreme cases, we may suppose the electron removed so suddenly that the other electrons have no time to change their position before it is out of their range of action, or to take the other extreme we may remove it so slowly that the electrons are always in their position of equilibrium corresponding to the position of the electron which is being ejected. In the first case the work required to move the electron away from the central positive charge is  $\frac{Ee}{r} - \frac{1}{2} \frac{Ce^2}{r^2}$ , and the work done by the other electrons in ejecting it is  $e^2/r_{12} + e^2/r_{13} + e^2/r_{14} \dots$  where  $r_{12}$ ,  $r_{13}$ ,  $r_{14}$  are the distances of the ejected electrons from the other electrons indicated by the suffixes 2, 3, 4. Now  $r_{12} = 2r \sin \theta_{12}$  where  $2\theta_{12}$  is the angle between the

<sup>4</sup> *Phil. Mag.*, 40, p. 169, 1920.



radii from the centre to the first and second electrons, and  $r$  is the distance of an electron from the centre, hence

$$\begin{aligned}\frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \dots &= \frac{1}{2r} \left( \frac{1}{\sin \vartheta_{12}} + \frac{1}{\sin \vartheta_{13}} + \frac{1}{\sin \vartheta_{14}} \dots \right) \\ &= \frac{1}{2r} S_n\end{aligned}\quad (7)$$

The work required to remove the electron is thus

$$\frac{Ee}{r} - \frac{1}{2} \frac{Ce^2}{r^2} - \frac{1}{2r} S_n \quad (8)$$

but from the equation of equilibrium

$$\frac{Ee}{r^2} - \frac{e^2C}{r^3} = \frac{e^2S_n}{4r^2}; \quad (9)$$

hence if  $V$  is the ionising potential,  $Ve$ , since it is equal to the work required to remove the electron, is given by the equation

$$Ve = \frac{Ee}{2} - \frac{3}{8} \frac{e^2S_n}{r}, \quad (10)$$

if  $n$  is the number of electrons  $E = ne$  and

$$V = \frac{e^2}{2r} \left( 1 - \frac{3}{4} S_n \right). \quad (11)$$

Next take the case when the electron is removed so slowly that the system of electrons is always in equilibrium. The work required is the difference between the potential energy of the atom in its original state when it contains  $n$  electrons and in its final state when it contains  $(n-1)$  electrons, the value of the former is

$$\frac{1}{2} \frac{ne^2}{r} \left( n - \frac{S_n}{4} \right) \quad (12)$$

that of the latter

$$\frac{1}{2} \frac{(n-1)e^2}{r_1} \left( n - \frac{S_{n-1}}{4} \right) \quad (13)$$

where  $r_1$  is the radius of the atom when one electron has been removed.

For the equilibrium of the electrons in this state we have

$$\frac{Ee}{r_1^2} - \frac{e^2C}{r_1^3} = \frac{e^2S_{n-1}}{4r_1^2} \quad (14)$$



from the equilibrium of the atom in its original state we have

$$\frac{Ee}{r^2} - \frac{e^2C}{r^3} = \frac{e^2S_n}{4r^2} \quad (15)$$

hence

$$\frac{1}{r_1} = \frac{1}{r} \frac{\left(1 - \frac{S_{n-1}}{4n}\right)}{1 - \frac{S_n}{4n}} \quad (16)$$

and the difference between the potential energies is

$$\begin{aligned} \frac{1}{2} \frac{e^2}{r} \left\{ n \left( n - \frac{S_n}{4} \right) - (n-1) \frac{\left( n - \frac{S_{n-1}}{4} \right)}{n - \frac{S_n}{4}} \right\} \\ = V_2 e \end{aligned} \quad (17)$$

if  $V_2$  is the ionising potential for slow ionisation. In calculating these ionising potentials we have assumed that the law of force between the positive charge and the electron was expressed by  $\frac{Ee}{r^2} - \frac{e^2C}{r^3}$  at all distances, there is evidence, however, that the repulsive term varying inversely as the cube of the distance has only a limited range of action and that beyond this range the force varies strictly as the inverse square of the distance. If we suppose that the range of the repulsive force is  $\rho Ce/E$ , then the work done in taking an electron from a distance  $r$  to an infinite distance will be

$$\begin{aligned} \int_r^\infty \frac{Ee}{r^2} dr - \int_r^{\rho Ce/E} \frac{e^2C}{r^3} dr \\ = \frac{Ee}{r} - \frac{1}{2} e^2 \frac{C}{r^2} + \frac{1}{2} \frac{E^2}{\rho^2 C} \end{aligned} \quad (18)$$

In calculating the ionising potential, we have neglected the last term and so have underestimated its value. Neglecting this correction, the ionising potentials for the elements whose outer layers contain 1, 2, 3, 4, 5, 6, 7, 8 electrons, respectively, are given in the following table.  $r_1$  is the radius of the outer layer of the one electron atom,  $r_2$  that of the two electron atom and so on. The third column gives the potential in volts when the values of  $r_1$  and  $r_2$ , given by W. L. Bragg (*loc. cit.*), are substituted in column 2.



TABLE V.

Number of Electrons in Outer Layer.	Ionising Potential for Quick Ionisation.	
1	$\frac{1}{2} e^2/r_1$	4.8 Lithium
2	$.625 e^2/r_2$	8.1 Beryllium
3	$.633 e^2/r_3$	
4	$.63 e^2/r_4$	11.8 Carbon
5	$.54 e^2/r_5$	12 Nitrogen
6	$.52 e^2/r_6$	12 Oxygen
7	$.5 e^2/r_7$	10.5 Fluorine
8		

These values apply to the ionisation of the atom and not of the molecule. In experiments on the ionising potential it is the value for the molecule and not for the atom which is in general determined.

#### SPECIFIC INDUCTIVE CAPACITY.

Further information about the atom is afforded by the study of the specific inductive capacity of the gas. We shall proceed to find the value of the specific inductive capacity of atoms containing different numbers of electrons.

The case of the one electron atom is exceptional because such an atom in its undisturbed state has a finite electrical moment, it will therefore tend to set in an electric field and this will give rise to a term in the specific inductive capacity independent of the displacement of the electrons inside the atom by the electric field; this term will vary rapidly with the temperature.<sup>5</sup> In addition to this effect due to the setting of the atoms there will be an effect due to the displacement of the electrons relative to the central core under the action of the electric field; this effect will be present in atoms containing more than one electron. The effect due to setting is absent when the normal atom has no finite electrical moment.

#### TWO ELECTRON ATOM.

If  $a$  is the distance of either of the electrons from the centre of the normal atom,  $X$  the external electric force, then if this force is in the direction of the line joining the electrons, the displace-

<sup>5</sup> *Phil. Mag.*, 27, p. 757.



ment  $\delta x$  of either of the electrons in the direction of the force is given by the equation

$$e\delta x = \frac{4}{5} a^3 X \quad (19)$$

This displacement of the electron relative to the positive charge endows the atom with an electric moment  $2e\delta x$ , and if  $N$  is the number of atoms per cubic centimetre, the electric moment per cubic centimetre is

$$N \frac{8}{5} a^3 X \quad (20)$$

hence if  $K_1$  is the specific inductive capacity of these atoms

$$K_1 - 1 = 4\pi N \frac{8}{5} a^3 \quad (21)$$

If the electric force acts at right angles to the line joining the electrons, then

$$e\delta x = 4a^3 X \quad (22)$$

and  $K_2$ , the specific inductive capacity for atoms orientated this way, is given by the equation

$$K_2 - 1 = 4\pi N \times 8a^3 \quad (23)$$

If the atoms in the gas are uniformly orientated, the specific inductive capacity  $K$  of the assemblage will be given by the equation

$$K = \frac{K_1 + 2K_2}{3}$$

or

$$K - 1 = 4\pi N a^3 \times \frac{8 \times 11}{15}. \quad (24)$$

The value of the specific inductive capacities for gases whose atoms contain from two to eight electrons is given in Table VI, which has been calculated by Miss Woodward.

It will be noticed that if  $K$  is the specific inductive capacity of a gas in the atomic condition,  $K$  is equal to  $ga^3$ , where  $a$  is the distance of the outer electrons from the centre of the atom,  $g$  is a quantity depending on the number of electrons in the outer layer. For elements belonging to the same family the number of electrons in the outer layer and therefore  $g$  is constant, so that the ratio of specific inductive capacities of two members of one family should be the same as the ratio of the volumes of the atoms. Cuthbertson has pointed out that there are some remarkably simple relations between the refractivities and therefore



between the values of  $K - 1$ , for consecutive elements in the same family. This is shown by Table VII given by Cuthbertson and Prideaux.<sup>6</sup>

Thus for these four families the ratio of the refractivity of an element in the first period to the corresponding element in the

TABLE VI.

*Specific Inductive Capacity of Atoms with Two to Eight Electrons.*

No. of Electrons	Arrangement.	$K$ .	Mean value of $K$ .
8	Cube	$1 + 4\pi r^3 N. 4'338$	$1 + 4\pi r^3 N. 4'338$
8	Twisted cube force perpendicular to sq. face	$1 + 4\pi r^3 N. 4'27$	
7	One layer force perpendicular to plane of pentagon	$1 + 4\pi Na^3. 3'605$	$1 + 4\pi a N. 4'29$
7	One layer force parallel to plane of pentagon	$1 + 4\pi Na^3. 4'634$	
6	One layer	$1 + 4\pi Nr^3. 4'269$	$1 + 4\pi r^3 N. 4'269$
5	One layer force perpendicular to plane of triangle	$1 + 4\pi a^3 N. 4'655$	$1 + 4\pi a^3 N. 4'236$
5	One layer force parallel to plane of triangle	$1 + 4\pi a^3 N. 4'027$	
4	Tetrahedron	$1 + 4\pi Nr^3. 3'9$	$1 + 4\pi Nr^3. 3'9$
3	Triangle force perpendicular to plane of triangle	$1 + 4\pi Nr^3. 5'203$	$1 + 4\pi Nr^3. 4'39$
3	Triangle force parallel to plane of triangle	$1 + 4\pi Nr^3. 3'981$	
2	Force perpendicular to line of electrons	$1 + 4\pi Nr^3. 8$	$1 + 4\pi Nr^3. 5'87$
2	Force parallel to line of electrons	$1 + 4\pi Nr^3. 1'6$	

second and third periods is the same for all the elements. We have seen that for members of the same family the ratio of the values of  $K - 1$  is equal to the ratio of the volumes of the elements. So from these experiments we arrive at the interesting deduction that, on passing from one period to the next, the volumes of all the atoms are increased in the same proportion.

<sup>6</sup> *Phil. Trans.*, A, 205, p. 319.



TABLE VII.

Element.	Refractivities	Approximate Ratio.
Helium .....	72.0	$\frac{1}{2}$
Neon .....	137.4	1
Argon .....	56.8	4
Krypton .....	85.0	6
Xenon .....	137.8	10
Fluorine .....	195	1
Chlorine .....	768	4
Bromine .....	1125	6
Iodine .....	1920	8
Nitrogen .....	297	1
Phosphorus .....	1197	4
Oxygen .....	270	1
Sulphur .....	1101	4

Some confirmation of this is furnished by the determinations by W. L. Bragg<sup>†</sup> of the diameters of the atom of the various elements, these were made by measuring by the Röntgen-ray method the distance between the metal and the negative element in a series of salts. In these the atoms of the negative elements are probably negatively charged and are not in the state of neutral atoms. For the electronegative elements the diameters are as follows:

$\text{\AA}$  is  $10^{-8}$  cm.

F = 1.35  $\text{\AA}$   
 Cl = 2.10  $\text{\AA}$   
 Br = 2.38  $\text{\AA}$   
 I = 2.8  $\text{\AA}$

O = 1.30  $\text{\AA}$   
 S = 2.05  $\text{\AA}$   
 Se = 2.35  $\text{\AA}$

C = 1.54  $\text{\AA}$   
 Si = 2.35  $\text{\AA}$

For the ratio of the diameters, we have

Cl/F = 1.55  
 S/O = 1.57  
 Si/C = 1.53

Br/F = 1.76  
 Se/O = 1.8

I/F = 2.07

For these elements, which are all electronegative ones, there seems thus some evidence from direct measurements that the ratio of the diameters of the atoms of corresponding elements in two

<sup>†</sup> *Phil. Mag.*, 40, p. 169.



periods is constant. It does not, however, apply to the electro-positive elements like the alkali metals. Thus, for example,

Na/Li = 1.185	K/Li = 1.38	Rb/Li = 1.5	
Mg/Be = 1.24	Ca/Be = 1.5	Sr/Be = 1.7	Ba/Be = 1.8

Thus the increase in the size of the atoms of corresponding metals in different periods is not nearly so large as in that of the atoms of corresponding electromagnetic elements.

(*To be continued.*)

---

**An Insect Enemy of Lead-covered Cables.**—Beetles that bore through lead cables but do not penetrate pure rubber have given much trouble in many parts of the United States. An important injury is that done to the lead sheathing of telephone cables in California. The beetles bore holes about one-tenth inch in diameter and moisture enters through these, causing short circuiting. One hole may put several hundred telephones out of use. The Bureau of Entomology has been making experiments in this matter which are summarized in a professional paper, Bulletin 1107, by R. D. Hartman, H. E. Burke and T. E. Snyder. The insect is able to penetrate any lead alloy so far used as sheathing and any poison or repellent, except that beef tallow will suffocate it and has been used with some success on the rings which suspend the cable since nearly all borrowing is done at this point. A new type of ring made of flattened steel wire, galvanized, is now being installed and it is believed that this will be an efficient method. In the meantime, the use of tallow is the most promising available. (*U. S. Department of Agriculture Service.*)

**Some Experiments on the Impact of Hydraulic Jets.** A. H. GIBSON and F. HEYWOOD. (*Phil. Mag.*, Jan., 1923.)—When a jet of water impinges on a hemispherical cup, the force exerted on the cup can readily be calculated, provided it be assumed that the liquid is deflected  $180^\circ$  on impact. But this theoretical force is never attained. The angle of deflection is not equal to two right angles and surface friction reduces the velocity of the discharge. Besides this there is often interference between the incoming and outgoing liquid. The actual force exerted is a certain fraction,  $k$ , of the calculated force. A series of experiments was made in which the ratio of the area of the cup to that of the jet varied from about two up to ten times as much. The value of the coefficient,  $k$ , rose rapidly as the ratio just defined was increased from 2 to about 3.8, where it attained its maximum value of from .8 to .9. With further increases of the ratio  $k$  slowly decreased. With a velocity of the jet of 20 ft. per sec. to get the greatest force on a cup the ratio of the area of this to that of the jet needs to be 20, while for 60 ft. per sec. it should be 11.5.

G. F. S.



# PERMALLOY, AN ALLOY OF REMARKABLE MAGNETIC PROPERTIES.\*

BY

H. D. ARNOLD, Ph.D.,

Member of the Institute

and G. W. ELMEN, M.A.

Research Laboratories,

American Telephone and Telegraph Company and Western Electric Company, Inc.

SOME years ago it was discovered in this laboratory that certain nickel-iron alloys, when properly heat-treated, possess remarkable magnetic properties.<sup>1</sup> These properties are developed in alloys which contain more than 30 per cent. of nickel and which have the face-centered cubic arrangement characteristic of nickel crystals, rather than the body-centered structure characteristic of iron. The entire range above 30 per cent. nickel exhibits these properties to some degree and offers new possibilities to those interested in magnetic materials.<sup>2</sup> The most startling results, however, are obtained with alloys of approximately 80 per cent. nickel and 20 per cent. iron, whose permeabilities at small field strengths are many times greater than any hitherto known. For convenience we call these peculiarly magnetic alloys by the general name "permalloy," which serves at the same time to recall their characteristic capability of attaining high initial permeability. The development of permalloy has assured us a revolutionary change in submarine cable construction and operation, and promises equally important advances in other fields of usefulness. It

---

\* Communicated by Brigadier General John J. Carty, Vice-president and Chief Engineer, American Telephone and Telegraph Company and Associate Editor of this JOURNAL.

<sup>1</sup> The present paper deals with the scientific aspects of these alloys. Some of their important commercial applications have been disclosed in patents, among which may be mentioned the following: Canada, No. 180,539, Nov. 20, 1917; Japan, No. 32,331, March 7, 1918; France, No. 533,432, Dec. 9, 1921; Great Britain, No. 188,688, Nov. 17, 1922.

<sup>2</sup> Permeabilities higher than that of iron have also recently been found at the lower end of this range by J. Würschmidt, *Phys. ZS.*, **23**, 499-500 (1922), and *ZS. f. Phys.*, **12**, 128-164 (1922); low hysteresis, coercivity, and remanence have been observed in the upper part of the range by T. D. Yensen, *J. Amer. Inst. Elect. Eng.*, **39**, 396-405 (1920); K. Zschiesche, *ZS. f. Phys.*, **12**, 201-214 (1922).



also presents questions of great interest to the scientist and emphasizes again the meagreness of our fundamental information about ferromagnetism. The present paper is intended to give a general discussion of the preparation and testing of permalloy, with sufficient detail to indicate its unusual characteristics. Detailed statements of numerical results are reserved for publication in separate articles dealing with specific properties.<sup>3</sup>

In making permalloy we use the purest commercial nickel and Armco iron. Our samples for laboratory study are prepared by melting these metals in a silica crucible, using a Northrup high-frequency induction furnace. The particular furnace which we use will conveniently melt a charge of about six pounds. An analysis typical of the resulting billets is as follows:

Ni .....	78.23
Fe .....	21.35
C .....	.04
Si .....	.03
P .....	trace
S .....	.035
Mn .....	.22
Co .....	.37
Cu .....	.10

The presence of other elements than nickel and iron is of course to be expected after any practical method of preparation. To determine their effects, samples were prepared in which the usual impurities were present in various proportions. It was found that their presence does affect the permeability of the alloys and that carbon is especially harmful. Since, however, the variations produced by slight changes in heat-treatment are very large compared with those due to small quantities of impurities we have found it unnecessary for most purposes to require higher purity than that indicated in the analysis above given.

In our laboratory studies we have made it a practice to reduce the billets through the forms of rod and wire to tape 3.2 mm. wide and 0.15 mm. thick. Accordingly test samples are available in a variety of forms and conditions. Thin narrow tape is

<sup>3</sup> L. W. McKeehan, "The Crystal Structure of Iron-Nickel Alloys," *Phys. Rev.* (2), 21 (1923).



particularly adapted to use in experiments involving heat-treatment, since it possesses a high ratio of area to volume and is easy to manipulate. Fortunately the entire nickel-iron series can be mechanically worked if sufficient care is exercised and we have thus been able to use samples of the same size, shape, and mechanical condition in all measurements upon which we have based comparisons between alloys. This practice has also made possible strictly comparable micrographic studies throughout the series.

Permeability is the magnetic characteristic of permalloy in which we first became interested and we have used its numerical value as an index in establishing the effects of mechanical and thermal treatments. Most of the measurements have been made in a ring permeameter of special design. The ring sample is prepared by winding twenty or more turns of tape around a disc about three inches in diameter. The disc is then removed, leaving the material in the form of a spirally laminated ring with a rectangular cross-section approximately 3.2 mm. by 6 mm. A single massive copper conductor is linked with this ring, and constitutes also the secondary of a transformer whose primary winding forms one arm of an inductance bridge. From the bridge measurements and the dimensions of the ring the permeability of the latter may readily be computed. For most of the measurements 112-cycle alternating current has been employed, permitting the use of telephone receivers in adjusting the balance of the bridge. The ring is sufficiently well laminated so that no serious troubles are introduced at this frequency by eddy currents. This fact was verified by making a number of permeability determinations at alternating current frequencies both above and below that chosen for routine use, and also by comparing the results of ring permeameter tests with those of ballistic tests on specially wound ring samples. The bridge method is particularly well adapted to the measurement of permeability in very weak magnetic fields since amplifiers may readily be used to increase the delicacy of the bridge adjustment to almost any degree desired. As a matter of convenience we have usually included in our test program measurements with fields of 0.002, 0.003, and 0.010 gauss, and on the graph of permeability against magnetizing field strength the straight line through these points has been extended to field



strength zero. We have called the permeability read from the graph at this point the "initial permeability" of the sample.

The form of permeameter used is especially adapted to making measurements quickly and with minimum handling of the sample, since it makes use of but a single magnetizing turn. The ring is laid on suitable insulating supports in an annular copper trough, and placing the copper cover on this trough completes the electrical circuit. In a modified instrument, the "hot permeameter," provided with a heating device, permeabilities may be measured from liquid air temperatures up to about  $1000^{\circ}$  C. without altering the position of the sample.

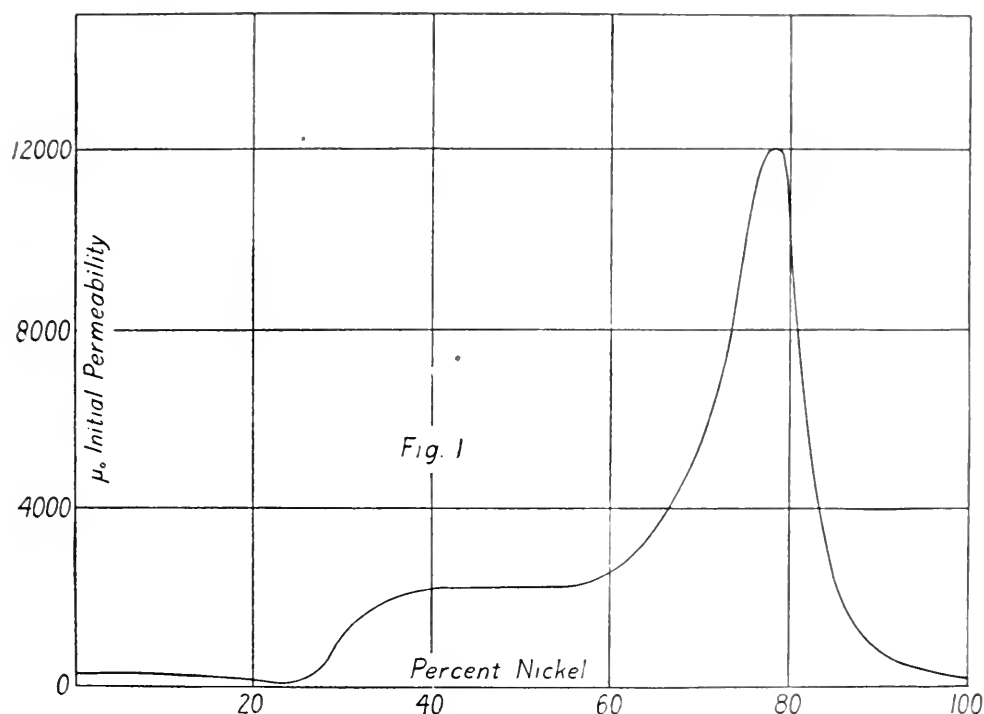
The heat-treatment of permalloy is of the utmost importance. To develop its maximum initial permeability it must be cooled not only through the proper temperature ranges, but also at the proper rates. It is obvious that only a small part of any sample can be given the most favorable treatment, since the interior portions of the sample cool at rates which are dependent upon the geometrical configuration and thermal properties of the material and are only indirectly under the control of the experimenter. For these reasons each shape and size of sample will have its own best heat-treatment and it is obviously difficult to establish the correct heat-treatment for a small element of volume, characteristic of permalloy as a material. By the use of thin tape, however, we secure fairly uniform treatment of the whole volume so long as the cooling is not too rapid, and fortunately the best cooling rate is not much different from the normal cooling rate of the tape in the open air. It has been found that temperature changes below  $300^{\circ}$  C. have very little effect upon the resultant properties of permalloy, but the rate of cooling from just above the magnetic transformation temperature down to about  $300^{\circ}$  C. is a controlling factor. By a long series of experiments a heat-treatment has been established which is especially well adapted to the permalloy test rings already described. They are first heated at about  $900^{\circ}$  C. for an hour and allowed to cool slowly, being protected from oxidation throughout these processes. They are then reheated to  $600^{\circ}$  C., quickly removed from the furnace and laid upon a copper plate which is at room temperature.

Not only does each size and shape of sample require its own



special heat-treatment, but samples differing only in composition also differ in their most suitable heat-treatments. In our investigation of the nickel-iron series we have not, however, attempted to determine the best heat-treatment for ring samples of each of the many alloys studied. By careful exploration we located the region about 80 per cent. nickel, 20 per cent. iron as the one promising the highest initial permeability and established the best heat-treatment for this composition. Keeping this treatment

FIG. 1.



unchanged we then relocated the best composition, finding it to be at about 78.5 per cent. nickel and 21.5 per cent. iron. There is a maximum temperature in the equilibrium diagram for this binary at about 70 per cent. nickel,<sup>4</sup> and it was natural to suspect that the maximum in initial permeability which we had found at 78.5 nickel might be displaced to 70 nickel by proper treatment. The 70 per cent. nickel alloy was accordingly subjected to a great variety of heat-treatments, but no method was found capable of producing in it an initial permeability as high as that readily obtainable in the 78.5 per cent. nickel alloy.

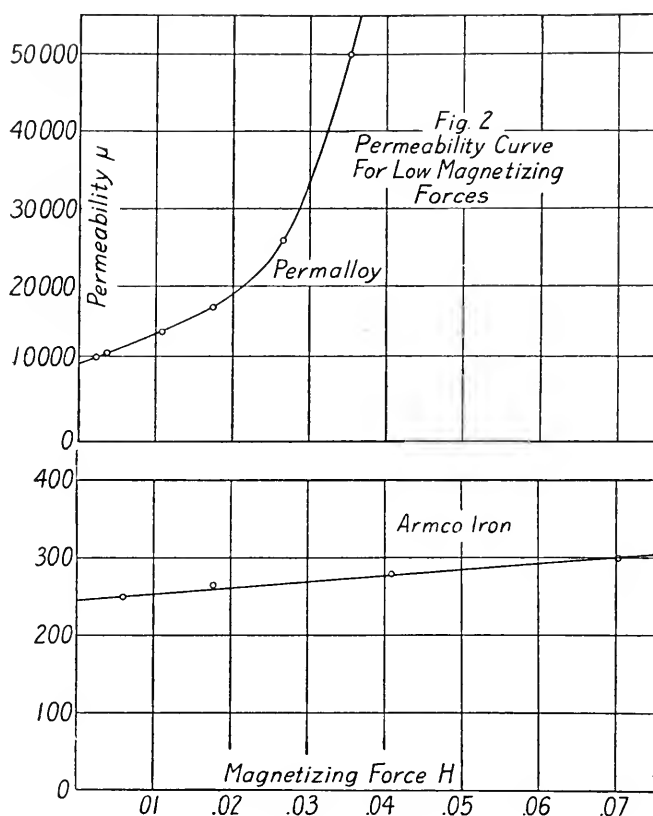
Fig. 1 shows the general way in which initial permeability has

<sup>4</sup> Bureau of Standards Circular No. 58, April 4, 1916.



been found to vary throughout the nickel-iron series when the heat-treatment determined as best for the 80 per cent. nickel alloy is used. It is obvious from what has been said above that too much weight must not be given to the actual values recorded at any composition. Had the best heat-treatment been determined for each sample the curve might have been altered considerably in detail, particularly outside the permalloy range. We believe, however, that its general form is approximately correct. Alloys were

FIG. 2.



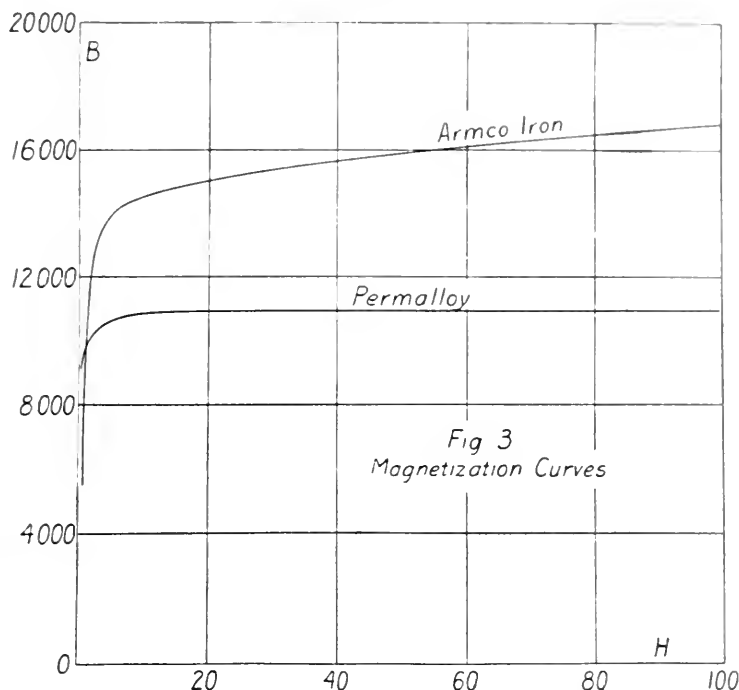
made at 5 per cent. steps throughout the range except in the vicinity of 80 per cent. nickel where a great number of slightly different compositions were investigated. The chemical analysis, rather than the intended composition, was used in every case, although the difference was never considerable.

The largest value of initial permeability for permalloy at room temperature which we have so far found in the ring permeameter is about 13,000, more than thirty times the corresponding value for the best soft iron. How extraordinary this is may be appre-



ciated by considering that this material, although it has a saturation value of magnetic intensity comparable with that of iron, approaches magnetic saturation in the earth's field. Unusual caution must therefore be exercised in measuring the properties of permalloy to protect the sample from the influence of stray magnetic fields. Fig. 2 shows, to different scales, the values of initial permeability in similar ring samples of permalloy and of

FIG. 3.



annealed Armco iron, and small portions of the corresponding  $\mu$ -H curves from which these were obtained.

We have measured the magnetization of permalloy at saturation and find that it is not sensitive to heat-treatment. The saturation values of magnetization per gram-atom are known to vary almost linearly with composition throughout the nickel-iron series, from 222 for iron to 59 for nickel.<sup>5</sup> The value 84 which we have found for the 78.5 per cent. nickel alloy is therefore not abnormal.

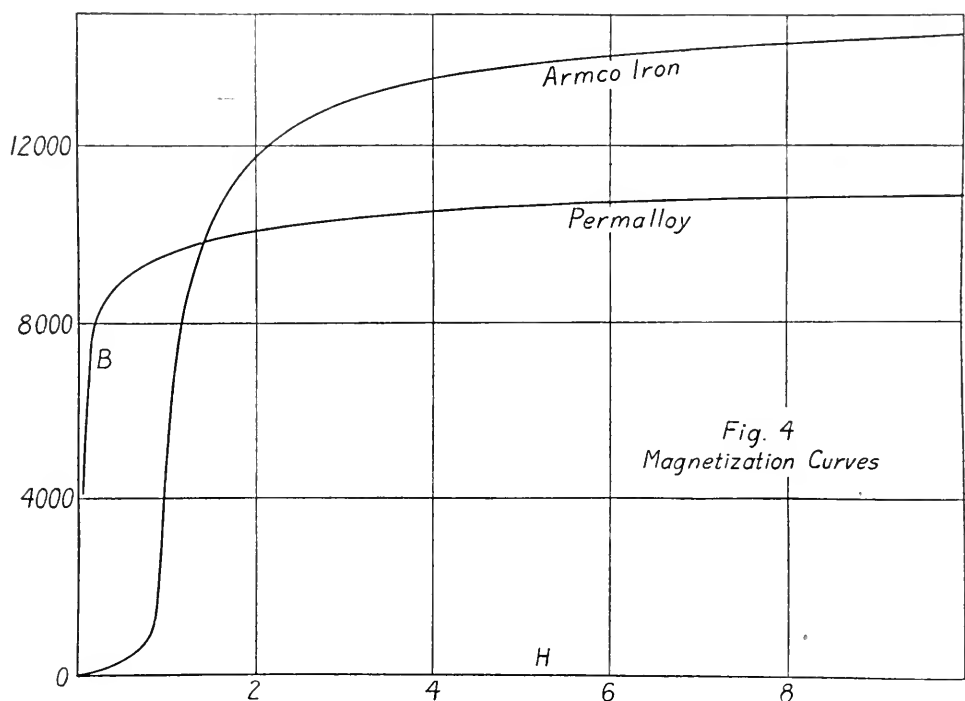
The magnetic characteristics of heat-treated ring samples of the same alloy have also been determined through a wider range of field strengths by ballistic methods. Figs. 3, 4, and 5 show

<sup>5</sup> P. Weiss, *Faraday Society Trans.*, 8, 149-156 (1912).



B-H curves for such a sample of permalloy and for a sample of annealed Armco iron. From Fig. 5 is apparent the enormous susceptibility of the former material in the weak fields so important in communication engineering. Fig. 6 shows for the same two materials hysteresis loops carried to a maximum induction of 5000 gauss. The area of the permalloy loop is only one-sixteenth that of the loop for soft iron. Fig. 7 shows the  $\mu$ -B curves for these materials. The maximum permeability here shown,

FIG. 4.



$\mu = 87,000$ , which is not exceptionally high for permalloy, largely exceeds the highest values obtainable in silicon steel.<sup>6</sup>

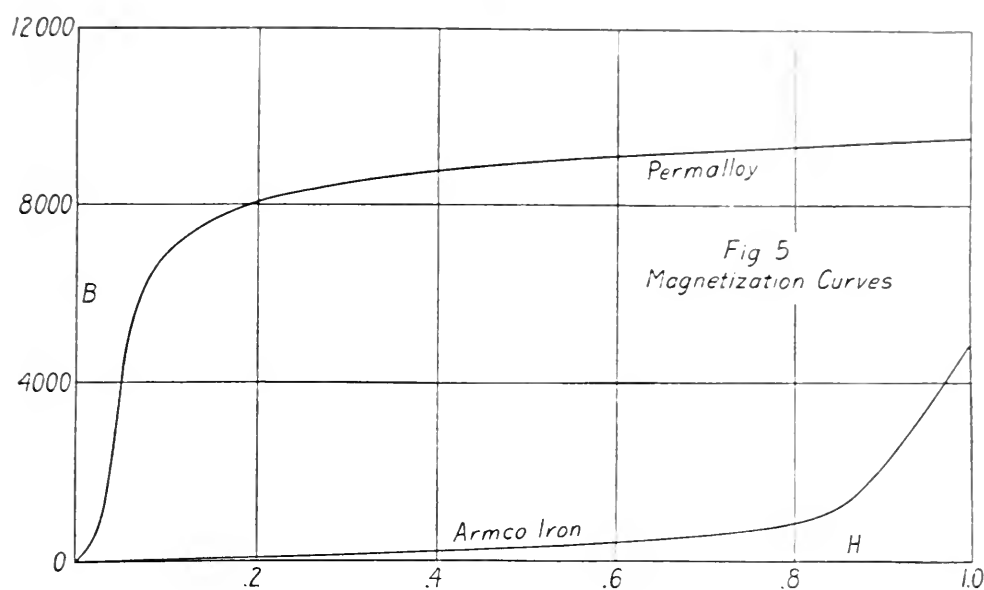
Early in the investigations it was found that heat-treated permalloy is sensitive to strain, and the routine measurements were so conducted as to avoid this disturbing effect. Separate investigations of the effects of strain upon permeability and electrical conductivity in straight samples, and of the converse effects of magnetization upon dimensions and conductivity were also undertaken. While these studies are not yet complete it can be stated that all these effects are large in comparison with the corresponding effects in hitherto available magnetic materials. So long as

<sup>6</sup> T. D. Yensen, U. S. Patent No. 1,358,810, Nov. 16, 1920.



the elastic limit of the material is not exceeded the effects due to strain are reproducible and disappear when the strain is relieved. The effects of magnetization, however, show the expected hysteretic properties. As an example of the magnitude of the effects producible it may be stated that between its value in the unstrained condition and about one-tenth that value the initial permeability of a heat-treated strip of certain of these materials can, by the mere variation of strain, be adjusted to any value we may for the

FIG. 5.



moment desire. The range through which the conductivity can similarly be adjusted by strain is much narrower, the maximum reduction being about 2 per cent.; which, however, is a large effect compared with that found in other metals.

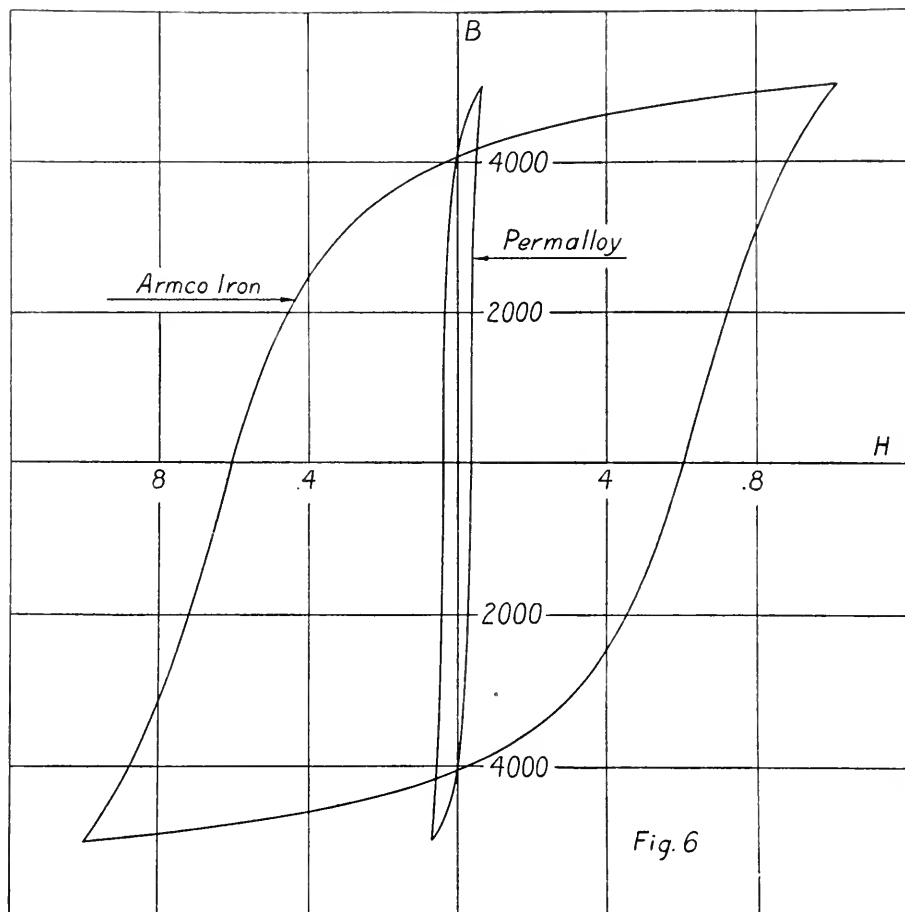
The effect of magnetization in reducing conductivity is as much as 2 per cent. for fields of the order of one gauss. This makes it easy, for example, to measure the earth's magnetic field to within about 1 per cent. by finding the strength of the opposing field necessary to give a permalloy strip its maximum conductivity. It will be noted that the conductivity change which we have mentioned as attainable by magnetization is the same as that attainable by elastic strain. This is no mere coincidence, for we find that the maximum change due to either cause alone is not further increased by superposition of the other, although the effects of small tensions and magnetizing fields are additive.



This suggests, of course, that both causes ultimately produce the same change in the mechanism responsible for conduction.

Since the effect of tension upon permeability is in some of these cases so marked it seemed surprising that the only reported study<sup>7</sup> of the converse effect, that is, of magnetostriction, indicated a zero value within the permalloy range. It appeared advisable therefore to study the magnetostriction of the series of alloys

FIG. 6.



here available. Preliminary results indicate that under usual conditions of experiment, heat-treated 78.5 per cent. nickel alloy exhibits larger magnetostriction than does iron.

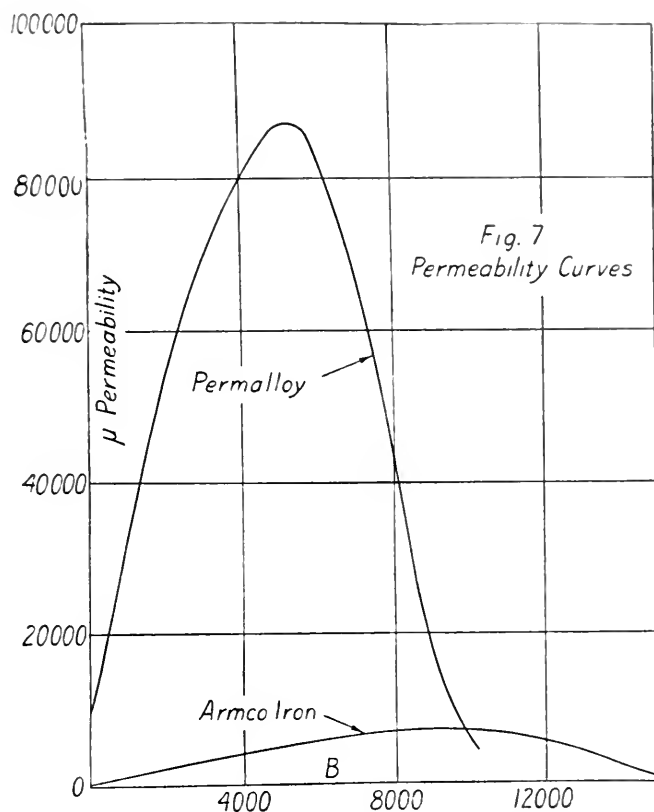
With the remarkable ferromagnetic behavior of permalloy in mind one naturally looks for analogous peculiarities in its other properties. As has been shown, however, the equilibrium diagram

<sup>7</sup> K. Honda and K. Kido, *Tohoku Univ. Sci. Rep.*, **9**, 221-232 (1920). It should be noted, however, that their alloys had received different treatments than ours.



does not point accurately to the composition exhibiting highest initial permeability. The conductivity curve is even less indicative of a peculiarity at this point, its minimum lying at about 35 per cent. nickel. The crystal structure is that of nickel and its type does not change until the nickel content is made less than 35 per cent. Even the mean spacing between adjacent atom-centres, and with it the density, varies continuously throughout the entire

FIG. 7.



range. Our experience in working these alloys also indicates that the series has no mechanical peculiarities at or near 80 per cent. nickel. Not only do these characteristics indicate no abnormality as the nickel content is increased beyond 70 per cent., but, what is more surprising, they are little affected by the heat treatments which so profoundly change the magnetic properties. So far as has been determined, therefore, it is only in connection with its magnetic properties that permalloy is unusual.

To the engineer the discovery of permalloy will mean the accomplishment of results heretofore believed impossible. For the scientist the principal interest in these materials may well lie



in the large response of their magnetic properties to simple external controls. Without alteration of composition these properties may be adjusted through extraordinary ranges by strain, by magnetization, or by heat-treatment. This allows a more definite study of the way in which these factors are related to magnetic properties than has been possible with materials hitherto available in which their effects are comparatively small and may be associated with complicated and irreversible changes in other properties. The behavior of permalloy demonstrates that ferromagnetism is associated with material structure in a different way than are the ordinary physical and chemical properties, and its extreme sensitiveness to control gives us a powerful method for use in magnetic investigations.

---

**Method of Separating Arc from Spark Lines in Emission Spectra.** W. WIEN. (*Ann. der Phys.*, No. 21, 1922.)—A few years ago the author found a way of observing luminous canal-rays even in the highest vacua. Upon this is based the method of distinguishing the two kinds of lines. A pencil of canal-rays enters a high vacuum through a narrow slit. The pressure in the vacuous space is kept low by a jacketing of solid  $\text{CO}_2$  or liquid air. The pencil passes between the plates of a tiny condenser, the small size of which is demanded by the condition that the rays must be still emitting light when they make their exit from the space between its plates. The several spectral lines are photographed by a train of lenses and prisms.

When hydrogen is used the photographs are just the same no matter whether the condenser is charged to a potential difference of 4500 volts or not. The lines photographed were those of the Balmer series. It follows therefore that these lines are emitted by uncharged atoms. Quite different results are obtained with oxygen as the gas. Most of the lines were deflected toward the negative plate by the application of the electrical field. These were members of the spark spectrum of the gas. Two lines belonging to the arc spectrum were not deflected. The former lines are due to charged atoms, the latter to uncharged ones.

With nitrogen not only lines but bands were in evidence. Of the lines eight belonging to the spark spectrum were deflected, while two of the arc spectrum were not affected. Four bands are deflected. These are customarily designated "negative bands" and are due to positively charged molecules. A much larger number of bands fails to be deflected. There is a marked difference between the deflected lines and the deflected bands. After deflection the canal-rays producing the lines still emit considerable light while those producing the negative bands give out scarcely any light.

No mercury lines are deflected.

G. F. S.



# A METHOD OF TRANSMITTING THE TELEGRAPH ALPHABET APPLICABLE FOR RADIO, LAND LINES, AND SUBMARINE CABLES.\*

BY

GEORGE O. SQUIER, K.C.M.G., D.S.M., Ph.D.

Major General, Chief Signal Officer of the Army.  
Associate Editor, Honorary Member of the Institute.

DUE to the rapid expansion of the use of radio telephony and telegraphy, the problem of interference, both natural and artificial, is becoming each day more and more pressing for solution. The conservation of the ether lanes is suddenly rising to international importance. In addition, the daily growing uses of radio for the solution of auxiliary problems such as range finding, navigation, beacons, etc., further serve to complicate the problem, and furthermore, it is believed that we are on the threshold of another development, *viz.*, photo-broadcasting, which will require and demand still additional ether channels to serve the public of the near future. It may be said, therefore, that the fundamental problem for the radio engineer is to devise methods to utilize these limited channels to the greatest extent possible, and to bend his efforts to the extension of their limits, both high and low.

In the case of artificial disturbances the chief offender, from an engineering standpoint, is the radio telegraph practice as it is universally conducted at present. Radio telephony and music of all classes have a form of modulation which is scientifically more sound than that of telegraphy. It is impossible at present to tune out the high-power radio telegraph stations, especially when a receiving station is in close proximity. Such stations, as at present operated, produce a veritable eruption in the ether, creating disturbances over a wide range of frequencies, and these serve to interfere with any form of radio receiver yet devised. Who has not experienced this in the operation of his radio receiving set? Radio telegraphic transmission, therefore, demands new consideration and new study from a scientific standpoint.

About eighty years ago Morse invented the telegraph alphabet of dots and dashes, and the modification of it, known as the International Morse, is now the universal method of international

---

\* Communicated by the Author.



radio telegraphy. This method is believed to be fundamentally unscientific, and the time has come to thoroughly consider a radical revision of the method of sending telegraphic messages. I do not here refer to an actual change at present in the Morse alphabet as regards the combinations of dots, dashes and spaces assigned to each letter, but I refer to the study of the correct method of sending these combinations in any circuit, whether radio, land lines, or submarine cables. The problem is the same in each of these three branches, but it is much more serious in radio for the reason of the necessary broadcasting properties thereof.

The rapid increase in the use of printing telegraphy makes it possible to further consider the telegraph alphabet from the standpoint of the number of the elements and the combinations thereof for each letter. This phase of the problem is now being studied by the Code Section of the Signal Corps.

In the Morse alphabet we find the principle of different time units for dots, dashes and spaces, as the basic idea of the system. In Standard Morse a dash is three times the length of time of a dot, and the spaces between letters and words are timed correspondingly.

These signals in International Morse are universally emitted into the ether from the transmitting antenna in the form of sudden interruptions in the antenna current, or sudden variations in this current. This method produces about the worst possible source of disturbances in the ether space for the reason, among others, that the disturbance has no regularity of any kind, and the speed of operating the sending key has a marked influence on the whole phenomena. Present practice is drifting away from the complete interruption of the antenna current which is the worst from an interference standpoint, but even the present methods of irregular and sudden variations of the current are still a long way from the possible scientific solution.

In 1915<sup>1</sup> the writer was considering the general problem of improving the transmission system for submarine cables, and in connection therewith gave study to a new form of alphabet suitable to such a circuit. The system devised at that time may be

---

<sup>1</sup> "On an Unbroken Alternating Current for Cable Telegraphy," *Proc. Phys. Soc. of London*, 27, Part V, August 15, 1915. U. S. Patent No. 1,233,519, July 17, 1917.



described briefly as a continuous wave system: "c.w." *versus* the "spark" system of the present cable practice. A method was developed of sending an unbroken alternating current through the cable, and means provided for interpreting this alternating current into intelligible signals. This system abandoned the Morse principle of different lengths of time for the signals as being fundamentally inefficient, and adopted the plan that all individual signal units should occupy equal lengths of time, and have equal importance, whether they were dots, dashes or spaces. The signals were distinguished by varying the intensity of the individual sending elements, *i.e.*, a dot, dash or space occupied equal time lengths, but were of different intensities. The variation in intensity for signaling was effected at the transmitter at the zero phase of the resultant current flowing into the cable, so that, theoretically, at the moment of any operation upon the current there was no current to operate upon.

A point of fundamental importance in this method is that no two adjacent signals are of the same sign, since each semicycle is utilized to effect signalling, giving a dot, dash or space. Other things being equal, the variations in intensities for each of the three elemental signals are reduced to a minimum on the theory that the minimum possible change of the fundamental wave should be made. The reason for this is that an alternating current in the steady state, which amounts to a series of the present cable letters "a" or "n" strung together without space, can attain a speed in any form of telegraphy many times greater than any practical system. A sinusoidal wave is transmitted through any form of electrical circuit without distortion of any kind, and, in fact, is the only type of wave that is so transmitted.

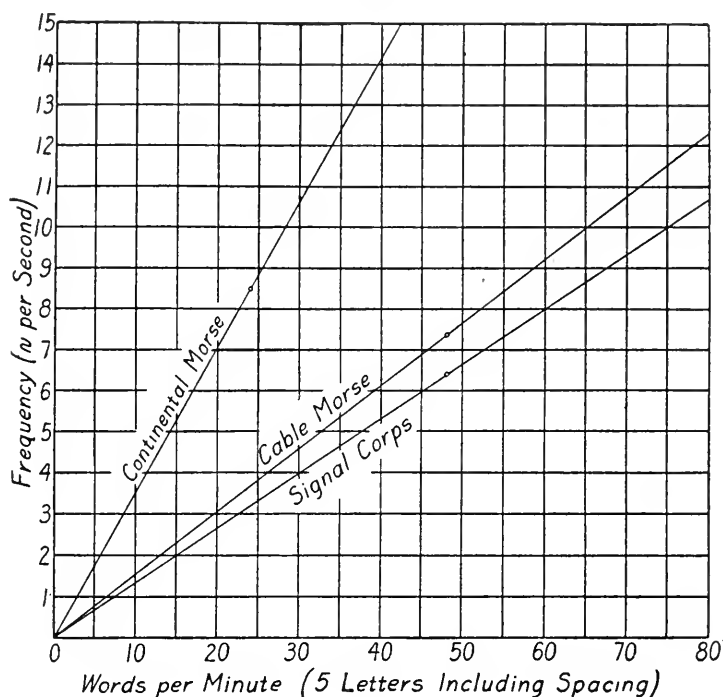
A still more important point to be considered is the transmission of the largest volume of telegraphic business with a minimum number of signals, and from this angle the new form of alphabet has most striking advantages.

Fig. 1 exhibits graphically the relative speeds of the International Morse alphabet, the present cable alphabet, and the alphabet proposed here. It will be noted that by the employment of the alphabet proposed here we gain immediately over 150 per cent. in the speed of transmission of signals; the ratio of 8.5 to 3.2, as shown in Fig. 1, is 2.65.



Referring to the cable Morse alphabet, the ratio of 3.67 to 3.2 does not indicate the real advantages of the proposed alphabet. In the present cable Morse alphabet, although the signals occupy equal lengths of time, some of the letters are transmitted by adjacent signals of the same sign. In letters such as "s" or "h," for instance, three and four consecutive signals have the same sign. The additional principle of the Signal Corps alphabet that

FIG. 1.



Infra-audio frequencies.

Note: Based on operating experiences with traffic in plain English text. Average time units per letter as follows: Continental Morse, 8.5; Cable Morse, 3.67; Signal Corps, 3.2; Ratio of 8.5 to 3.2=2.65.

no two consecutive signals shall be of the same sign permits, for the first time, a continuous wave of one definite frequency being employed for the alphabet. This makes it possible to utilize, effectively, electrical and mechanical tuning, either or both.

Fig. 2<sub>B</sub> illustrates graphically this method of modulating a single frequency wave, and shows the words "Now is the time" as they would be transmitted by this method, in which we arbitrarily assign the largest amplitude for a dash, the next size amplitude for a dot, and the smallest for the spaces between.

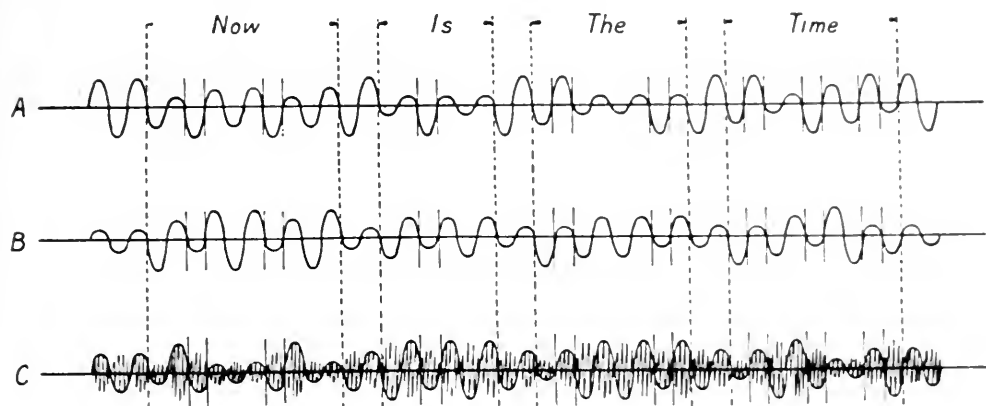
Figs. 2<sub>A</sub> and 2<sub>C</sub> show two other combinations.



The particular combination  $2_B$  has been tried out in actual practice on cables, and has been tested by the engineers of the British Post Office.

If we consider the present method of operating the large radio telegraph stations we find that the method of sending, whether automatic or by hand, has no relation to the phase of the current flowing in the antenna, with the result that in the ordinary transmission of a message the large current flowing in the antenna, sometimes as much as two or three hundred amperes, is suddenly

FIG. 2.



(A) Dot—smallest amplitude. Dash—medium amplitude. Space—largest amplitude.  
 (B) Space—smallest amplitude. Dot—medium amplitude. Dash—largest amplitude.  
 (C) Dash—smallest amplitude. Space—medium amplitude. Dot—largest amplitude.  
 There are three other possible permutations of amplitudes not shown here. Ratio of amplitudes of signalling units arbitrarily assumed as 1: 2: 3.

interrupted or changed in a perfectly haphazard manner. The transmitting key is closed or opened at any indefinite point of phase, with the result that in the same letter or message a large flow of current is interrupted or changed at all possible values from zero to a maximum, positive or negative.

It is well known that the sudden breaking or introduction of high impedances in an alternating current circuit produces transient phenomena which results in a whole group of harmonics being transmitted. Add to this the practical condition of performing this operation upon a current ranging all the way from zero to hundreds of amperes, and it is easily seen that the ether of space is bombarded with a mass of frequencies never twice alike even in the same letter. It is little wonder, therefore, that no method has yet been devised to prevent such a disturbance from interfering radically with the reception of radio signals. Entirely



apart, therefore, from a gain of over 150 per cent. in the transmission speed, from an interference standpoint the present method is about as bad as it could well be.

The other source of disturbances in radio is natural disturbances, generally designated as "static" or "atmospherics." Here again it is believed that the solution may be found in the method of sending proposed here, for the reason that the modulating frequencies employed are of a very low order, and it should be comparatively simple to devise instrumentalities which will enable us to differentiate between these low modulating frequencies and the higher frequencies of the "static" or any other natural disturbance. To emphasize my point, by an examination of Fig. 1 it is seen that a modulating frequency as low as 10 per second, which is a very high frequency for ocean cable practice, corresponds to 75 words a minute, which is far higher than any form of sound reception. A modulating frequency of 60 cycles per second, the normal power frequency, corresponds to a speed of 450 words a minute, of 5 letters each.

If this speed, for traffic reasons, is too great, it is only necessary to make the same perforations in the transmitting tape correspond to a suitable even multiple of a semicycle to reduce the speed to any desired value. For instance, by making each of the signalling units correspond to six complete cycles of current instead of one semicycle, the speed of signalling is reduced to  $37\frac{1}{2}$  words a minute, a commercial speed of signalling. In this method of using the alphabet, wave trains are employed as the signalling elements.

The ratio of the lowest frequencies employed in radio to the modulating frequencies here considered is of the order of thousands.

At present the radio engineer has utilized and made his own all of the audio-frequency range and at least several octaves of the radio-frequency range, and has devised apparatus for the amplification and rectification of both of these ranges, audio and radio. This plan proposes to enter the unused infra-audio range, which would not only add a most useful band of frequencies to those now used, but would give a band below the range of the human ear. If this band were employed for telegraphy, an additional advantage would be that it could not interfere with any radio



receiving. This method of eliminating interference would be most effective.

Finally, it is seen that by the method proposed here it is possible to modulate a single radio frequency by a number of modulating frequencies, and thus multiply the capacity of each radio frequency channel.

In 1921 the writer attended at Paris an international technical conference on outstanding radio problems, and for two months special delegates of the five great powers gave consideration to technical points connected with international radio telephony and telegraphy. Such matters as interference, logarithmic decrements, disposition and allocation of wave-lengths, radiation, etc., were considered. It is now proposed that the general subject of a suitable method for transmitting telegraphic signals either for radio, land lines or submarine cables be considered at the next international technical conference, with a view, if possible, of unifying all branches of telegraphy using the same system of modulation for the signals.

Office of the Chief Signal Officer,  
War Department,  
Washington, D.C.,  
March 6, 1923.

---

**A Problem in Viscosity: The Thickness of Liquid Films Formed on Solid Surfaces Under Dynamic Conditions.** F. S. GOUCHER and H. WARD. (*Phil. Mag.*, Nov., 1922.)—"In many important industrial processes solid surfaces are coated with a layer of liquid by drawing them out of a bath of the liquid. The enamelling of wires or tubes is such a process, and so in all essentials is painting with a brush. We are aware of no theory or even complete experimental investigation directed to determine how the thickness of the liquid layer produced in such circumstances varies with the properties of the liquid, the solid surface, the velocity of drawing, and other possible factors. The experiments described in this paper show that the matter is surprisingly simple." Let us consider a very wide sheet of solid material being drawn with constant velocity vertically upward out of a liquid. Since observation shows that the thickness of the layer of liquid adhering is, at least under certain conditions, constant for considerable distances above the surface of the liquid, it follows that the motions of the layers of adhering liquid must be in vertical planes parallel to the solid. Deviation from vertical motion would cause a change in the thickness of the film. The solid is moving upward and drags with it at the same velocity the layer of



liquid adjacent to it. This layer viscously drags the layer next to it, but this does not move upward with the velocity of the solid owing to the force of gravity. As we give attention to layers farther and farther distant from the solid, we find them moving upward with less and less velocity. The surprising conclusion is reached that the outermost layer is neither rising nor sinking. Since the forces due to viscosity and to gravity are the only forces acting on the layers of liquid, and since they produce a steady state of flow, it follows that they just balance each other. After solving the appropriate differential equations this relation is derived,  $t^2 = \frac{2v_0\eta}{\rho g}$ , where this thick-

ness of adhering liquid,  $v_0$  is velocity of solid,  $\rho$  is density of liquid and  $\eta$  its coefficient of viscosity. No property of the material forming the solid appears in the formula.

A study of the coating of wax forming upon copper strips was made. The actual thickness of the layer was usually somewhat greater than the value calculated from the constants of the liquid wax. This is due to the fact that as soon as a layer of molten wax is drawn out of the main body of the liquid its temperature falls and in consequence of this the viscosity grows greater.

When tubes are used surface tension comes into play. On the outside of the tube the contraction of the surface of the liquid acts along with gravity to make the layer thinner, while inside of the tube these two forces are in antagonism. Hence the thickness of the layer within the tube is greater than that outside of it. G. F. S.

**Franklin Bache.**—DR. EDGAR F. SMITH has published a brochure on "Franklin Bache, Chemist," in his series of treatises on the history of chemistry in America. Doctor Bache, who was a great-grandson of Benjamin Franklin, was an early member of The Franklin Institute, having been elected to membership in 1827. He was professor of chemistry in the Jefferson Medical College and the Philadelphia College of Pharmacy, founded the United States Dispensary, and prepared for publication the treatise of James Cutbush, entitled "A System of Pyrotechny," after the death of Cutbush. In 1841, Bache stressed the great importance of chemistry in its applications to medicine and pharmacy. J. S. H.

**The Electrical Resistance of a Rotating Coil.** A. P. CARMAN. (*Phys. Rev.*, April, 1922.)—Maxwell stated that "the electric current has a true momentum." A coil of "advance" wire, wound upon a disc, was rotated at 7000 r.p.m. about the axis of the disc, in order to see whether the rotation would throw the current away from the axis and into the outer parts of the coil. Such a redistribution of the current should manifest itself by an increase in the resistance of the coil. In spite of a peripheral speed of 10 km. per sec., an increase of resistance of merely one part in 100,000 was obtained. Even this may be attributed to other causes. G. F. S.



## ELECTRIC FILTER CIRCUITS.\*

BY

LOUIS COHEN, Ph.D.

Consulting Engineer, Signal Corps, U.S.A.

THE theory and operation of electric filter circuits, the invention of Dr. G. A. Campbell, has been discussed in several able papers by Doctor Campbell himself and others. A very clear exposition of the fundamental principles of electric filter circuits and the working out of many design formulas are given by Doctor Campbell in the two patents issued to him in 1917.<sup>1</sup>

In all the discussions of the subject, however, the problem is considered from the standpoint of an artificial line, and creates the impression that an electric filter circuit, which, as is well known, consists of a number of circuits connected together in various forms, involves a new principle and the theory of it is different from that applied to ordinary coupled circuits. It is true that when an electric filter circuit is made up of a large number of independent circuits it assumes the character of an artificial line, having certain characteristics governed by the arrangement of the inductance and capacity in each individual circuit. But is it justifiable to consider the problem from the standpoint of an artificial line when only a very limited number of circuits or sections is used, say two or three sections only, and if not, what are the limiting conditions, what is the minimum number of sections required for the system to acquire the characteristic properties of an electric filter, that is, to permit band frequency tuning? And if the number of sections is below the minimum number required, can we obtain band frequency tuning in any degree whatsoever? The answers to these questions are not obvious

---

\* Communicated by Major General George O. Squier, Chief Signal Officer, U.S.A., and Associate Editor of this JOURNAL.

<sup>1</sup> See U. S. Patents Nos. 1,227,113 and 1,227,114 issued to Dr. G. A. Campbell, May 22, 1917.

"Physical Theory of Electric Wave Filter," by G. A. Campbell, *The Bell System Technical Journal*, November, 1922.

"Theory and Design of Uniform and Composite Electric Wave Filters," by Otto J. Zobel, *The Bell System Technical Journal*, January, 1923.



when the problem is considered from the viewpoint of an artificial line, and certainly it is not at all clear when the problem is treated in that light as to the extent of improvement in band tuning obtained as the number of sections used is gradually increased.

It is believed that the whole problem is much simplified and the interpretation of the physical principles governing the operation of the electric filter circuit is more easily understood in considering the problem from the standpoint of coupled circuits. After all, an electric filter is nothing more, of course, than a number of independent circuits joined together electrically. The connection between the individual circuits may be either direct or through any other type of coupling, and there does not seem to be any reason why the problem should not be considered from the standpoint of coupled circuits, and thus enable us to see clearly what may be expected in the matter of frequency tuning from a system of circuits of any number of sections whatsoever, say two, three, or more, and also obtain some information of the improvement or change in conditions as the number of circuits used is gradually increased. Strictly speaking, it is only when the number of sections used is infinitely large that the system may be considered as an artificial line, and this condition is only approximated when a finite number of sections is used. By considering the problem from the standpoint of coupled circuits, we should be able to see how closely we approximate the condition of an infinite number of sections when only a limited number of sections or independent circuits is used.

In what follows I have considered, first, a system of electromagnetically coupled circuits and have shown that strictly band tuning is obtained only when an infinite number of independent circuits is used, but that the condition of band tuning is closely approximated when a limited number of sections is employed. From the theory given here, curves could be easily plotted for any particular case, showing the deviation from the uniform band tuning for any limited number of circuits.

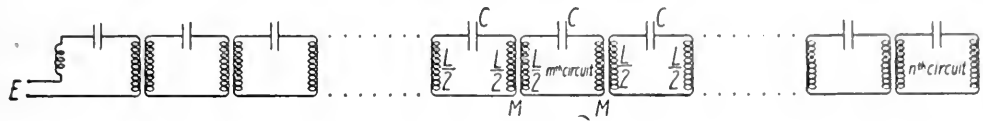
I also apply the same considerations to a system of direct connected circuits the usual arrangements employed in the design of electric filter circuits.

For a system of circuits consisting of  $n$  circuits coupled electromagnetically, as shown in Fig. 1, a sine e.m.f.  $Ee^{j\omega t}$



impressed on first circuit, we have the following system of equations:

FIG. 1.



$$\left. \begin{aligned} ZI_1 + Mj\omega I_2 &= E\epsilon^{j\omega t}, \\ ZI_2 + Mj\omega I_1 + Mj\omega I_3 &= 0, \\ \dots\dots\dots \\ ZI_m + Mj\omega I_{m-1} + Mj\omega I_{m+1} &= 0, \\ \dots\dots\dots \\ ZI_n + Mj\omega I_{n-1} &= 0 \end{aligned} \right\} \tag{1}$$

$Z$  is the impedance of each of the circuits and  $M$  is the mutual inductance between any two adjacent circuits. All the equations except the first and the last are satisfied by the following solution:

$$I_m = A \epsilon^{m\gamma} + B \epsilon^{-m\gamma}. \tag{2}$$

Substituting in (1) we have

$$Z(A\epsilon^{m\gamma} + B\epsilon^{-m\gamma}) + Mj\omega(A\epsilon^{(m-1)\gamma} + B\epsilon^{-(m-1)\gamma} + A\epsilon^{(m+1)\gamma} + B\epsilon^{-(m+1)\gamma}) = 0, \tag{3}$$

or

$$A\epsilon^{m\gamma}\{Z + Mj\omega\epsilon^{-\gamma} + Mj\omega\epsilon^{\gamma}\} + B\epsilon^{-m\gamma}\{Z + Mj\omega\epsilon^{\gamma} + Mj\omega\epsilon^{-\gamma}\} = 0, \tag{4}$$

and all the equations of (1) are satisfied by the above solution if we assign to  $\gamma$  such a value as to satisfy the relation

$$Z + Mj\omega(\epsilon^{\gamma} + \epsilon^{-\gamma}) = 0,$$

or

$$\epsilon^{\gamma} + \epsilon^{-\gamma} = -\frac{Z}{Mj\omega}. \tag{5}$$

The constants  $A$  and  $B$  of the solution given by (2) are determined from the first and last equations of (1). We have in this case

$$\left. \begin{aligned} Z(A\epsilon^{\gamma} + B\epsilon^{-\gamma}) + Mj\omega(A\epsilon^{2\gamma} + B\epsilon^{-2\gamma}) &= E\epsilon^{j\omega t}, \\ Z(A\epsilon^{n\gamma} + B\epsilon^{-n\gamma}) + Mj\omega(A\epsilon^{(n-1)\gamma} + B\epsilon^{-(n-1)\gamma}) &= 0. \end{aligned} \right\} \tag{6}$$



The values of  $A$  and  $B$  are readily determined from the above two equations as follows:

$$\left. \begin{aligned} A &= \frac{E\varepsilon^{j\omega t} \varepsilon^{-n\gamma} (Z + Mj\omega\varepsilon^\gamma)}{\varepsilon^{-(n-1)\gamma} (Z + Mj\omega\varepsilon^\gamma)^2 - \varepsilon^{-(n-1)\gamma} (Z + Mj\omega\varepsilon^{-\gamma})^2}, \\ B &= \frac{E\varepsilon^{j\omega t} \varepsilon^{n\gamma} (Z + Mj\omega\varepsilon^{-\gamma})}{\varepsilon^{-(n-1)\gamma} (Z + Mj\omega\varepsilon^\gamma)^2 - \varepsilon^{-(n-1)\gamma} (Z + Mj\omega\varepsilon^{-\gamma})^2}. \end{aligned} \right\} \quad (7)$$

Taking into account the relation given by (5) the above reduce to

$$\left. \begin{aligned} A &= \frac{E\varepsilon^{j\omega t} \varepsilon^{-(n+1)\gamma}}{Mj\omega(\varepsilon^{(n+1)\gamma} - \varepsilon^{-(n+1)\gamma})}, \\ B &= \frac{E\varepsilon^{j\omega t} \varepsilon^{(n+1)\gamma}}{Mj\omega(\varepsilon^{(n+1)\gamma} - \varepsilon^{-(n+1)\gamma})}. \end{aligned} \right\} \quad (8)$$

Substituting these values in (2) we get the complete expression for the current in any circuit, say the  $m$ th circuit, as follows:

$$I_m = \frac{E\varepsilon^{j\omega t} \{ \varepsilon^{(m-n-1)\gamma} - \varepsilon^{-(m-n-1)\gamma} \}}{Mj\omega \{ \varepsilon^{(n+1)\gamma} - \varepsilon^{-(n+1)\gamma} \}}. \quad (9)$$

For the last circuit,  $m = n$

$$\begin{aligned} I_n &= \frac{-E\varepsilon^{j\omega t} \{ \varepsilon^\gamma - \varepsilon^{-\gamma} \}}{Mj\omega \{ \varepsilon^{(n+1)\gamma} - \varepsilon^{-(n+1)\gamma} \}}, \\ &= \frac{-E\varepsilon^{j\omega t} \sinh \gamma}{Mj\omega \sinh (n+1)\gamma}. \end{aligned} \quad (10)$$

Obviously the current is of maximum value when the value of  $\gamma$  is such as to give the denominator a minimum value. If we neglect the resistance, the denominator of equation (12) is the reactance of the system and is of zero value when adjusted for resonance condition.

For

$$\begin{aligned} \sinh (n+1)\gamma &= 0, \\ (n+1)\gamma &= js\pi, s = 0, 1, 2, 3, \dots \\ \gamma &= \frac{js\pi}{n+1}. \end{aligned} \quad (11)$$

The function  $\sinh (n+1)\gamma$  is zero for all integer values of  $s$  from zero to infinity, but the zero value of  $s$  and the values above  $n$  are to be disregarded because for  $s = 0$  the numerator in the expression for the current given by (10) also becomes zero, and the current therefore is not a maximum for  $s = 0$ ; also for values



of  $s > n$  we get a repetition of the values obtained from assigning to  $s$  the values from 1 to  $n$ , and nothing is contributed by using the values of  $s > n$ .

For two coupled circuits we have only two values of  $\gamma$

$$\begin{aligned}\gamma_1 &= j \frac{\pi}{3}, \\ \gamma_2 &= j \frac{2\pi}{3}.\end{aligned}\tag{12}$$

For three coupled circuits there are three values of  $\gamma$

$$\begin{aligned}\gamma_1 &= j \frac{\pi}{4}, \\ \gamma_2 &= j \frac{2\pi}{4}, \\ \gamma_3 &= j \frac{3\pi}{4}.\end{aligned}\tag{13}$$

Similarly for  $n$  coupled circuits  $n$  values of  $\gamma$ .

The frequencies for which the system is in resonance are determined from the relation given by (5). Substituting the values of  $\gamma$  from (11) in (5) we get the following:

$$2 \cos \frac{s\pi}{n-1} = - \frac{Z}{Mj\omega}.\tag{14}$$

If the reactance of each circuit is simply that of an inductance and capacity in series,  $Z = Lj\omega + \frac{1}{Cj\omega}$ , (14) takes the form

$$2 \cos \frac{s\pi}{1-n} = - \frac{L}{M} \left( 1 - \frac{1}{LC\omega^2} \right).\tag{15}$$

Solving for  $\omega$  we obtain

$$\omega^2 = \frac{1}{LC \left( 1 + \frac{2M}{L} \cos \frac{s\pi}{n-1} \right)}.\tag{16}$$

By assigning to  $s$  all the values from 1 to  $n$ , we get the values of the resonance frequencies of the system, which are, of course, also the free vibration frequencies of the system.

For two coupled circuits we have by (16)

$$\left. \begin{aligned}\omega_1 &= \frac{1}{\sqrt{LC \left( 1 + \frac{M}{L} \right)}}, \\ \omega_2 &= \frac{1}{\sqrt{LC \left( 1 - \frac{M}{L} \right)}}.\end{aligned} \right\}\tag{17}$$



For three coupled circuits

$$\left. \begin{aligned} \omega_1 &= \frac{1}{\sqrt{LC \left(1 + \frac{M\sqrt{2}}{L}\right)}}, \\ \omega_2 &= \frac{1}{\sqrt{LC}}, \\ \omega_3 &= \frac{1}{\sqrt{LC \left(1 - \frac{M\sqrt{2}}{L}\right)}}. \end{aligned} \right\} \quad (18)$$

For four coupled circuits, the four values of  $\omega$  are

$$\left. \begin{aligned} \omega_1 &= \frac{1}{\sqrt{LC \left(1 + 1.618 \frac{M}{L}\right)}}, \\ \omega_2 &= \frac{1}{\sqrt{LC \left(1 + 0.618 \frac{M}{L}\right)}}, \\ \omega_3 &= \frac{1}{\sqrt{LC \left(1 - 0.618 \frac{M}{L}\right)}}, \\ \omega_4 &= \frac{1}{\sqrt{LC \left(1 - 1.618 \frac{M}{L}\right)}}. \end{aligned} \right\} \quad (19)$$

It is obvious from the above that the current in a system of coupled circuits as a function of frequency will have a number of maxima corresponding to the number of circuits. As the number of circuits is increased these maxima come closer and closer together, and for a large number of circuits they practically coalesce and the system is in resonance for the entire range of frequencies from  $\omega_1$  to  $\omega_n$ , and this gives the effect of band tuning. Even for a limited number of circuits the maxima are not far apart and the system approximates the condition of band tuning. It is evident from the expression for  $\omega$  given by (16) that the difference between the extreme frequencies corresponding to  $\omega_1$  and  $\omega_n$  becomes greater as the number of circuits is increased. In the limit when the number of circuits is infinite, the extreme frequencies have the following values:

$$\left. \begin{aligned} f_1 &= \frac{\omega_1}{2\pi} = \frac{1}{2\pi\sqrt{LC \left(1 + \frac{2M}{L}\right)}}, \\ f_n &= \frac{\omega_n}{2\pi} = \frac{1}{2\pi\sqrt{LC \left(1 - \frac{2M}{L}\right)}}. \end{aligned} \right\} \quad (20)$$



In a limited number of electromagnetically coupled circuits the width of the frequency band is always less than the frequency difference  $\omega_1 - \omega_n$  given by the values of  $\omega_1$  and  $\omega_n$  above, approaching this condition as the number of circuits is indefinitely increased.

Considering the problem from the standpoint of an artificial line, the number of circuits large to give the equivalent condition of a line, we make use of equation (5)

$$\epsilon^\gamma + \epsilon^{-\gamma} = \frac{-Z}{Mj\omega}. \quad (5)$$

Put for convenience

$$\frac{Z}{2Mj\omega} = K, \quad (21)$$

and solve for  $\epsilon^\gamma$  and  $\epsilon^{-\gamma}$ , we obtain

$$\left. \begin{aligned} \epsilon^\gamma &= -K + \sqrt{K^2 - 1}, \\ \epsilon^{-\gamma} &= -K - \sqrt{K^2 - 1}. \end{aligned} \right\} \quad (22)$$

If  $K^2 < 1$ , that is

$$-1 < K < 1, \quad (23)$$

$$\left. \begin{aligned} \epsilon^\gamma &= -K + j\sqrt{1 - K^2}, \\ \epsilon^{-\gamma} &= -K - j\sqrt{1 - K^2}. \end{aligned} \right\} \quad (24)$$

Put  $\gamma = \alpha + j\beta$ , and the above equations take the form

$$\left. \begin{aligned} \epsilon^\alpha (\cos \beta + j \sin \beta) &= -K + j\sqrt{1 - K^2}, \\ \epsilon^{-\alpha} (\cos \beta - j \sin \beta) &= -K - j\sqrt{1 - K^2}. \end{aligned} \right\} \quad (25)$$

From either of the above equations, we get the values of  $\alpha$  and  $\beta$  as follows:

$$\begin{aligned} \epsilon^\alpha &= \epsilon^{-\alpha} = 1, \\ \cos \beta &= -K, \end{aligned}$$

that is

$$\left. \begin{aligned} \alpha &= 0, \\ \beta &= \cos^{-1}(-K). \end{aligned} \right\} \quad (26)$$

For values of  $K$  between the limits  $-1$  and  $+1$  as given by (23), the attenuation is zero, no reduction in intensity of the current as it passes from one circuit to another. The range of frequencies for which there is no attenuation can be readily deter-



mined from the relation  $K = \pm 1$ . If each circuit consists of an inductance and capacity in series, we have

$$K = \frac{-Z}{2Mj\omega} = \frac{-Lj\omega}{Mj\omega} \left( 1 - \frac{1}{LC\omega^2} \right) = \pm 1, \quad (27)$$

and

$$\omega^2 = \frac{1}{LC \left( 1 \pm \frac{2M}{L} \right)}. \quad (28)$$

That is, the band of frequencies for which there is no attenuation lies in the frequency region, the limits of which are

$$\left. \begin{aligned} f_1 = \frac{\omega_1}{2\pi} &= \frac{1}{2\pi \sqrt{LC \left( 1 + \frac{2M}{L} \right)}}, \\ f_n = \frac{\omega_n}{2\pi} &= \frac{1}{2\pi \sqrt{LC \left( 1 - \frac{2M}{L} \right)}}. \end{aligned} \right\} \quad (29)$$

The same result as given by equations (20).

For  $\frac{M}{L} = \frac{1}{2}$ , equations (20) or (29) reduce to

$$\left. \begin{aligned} f_1 &= \frac{1}{2\pi \sqrt{2LC}}, \\ f_n &= \infty. \end{aligned} \right\} \quad (30)$$

The system is in resonance for all frequencies above  $f_1$ , permitting currents of all these frequencies to pass without attenuation. From the standpoint of coupled circuits this result may be interpreted as the reactance of the system being zero for all frequencies within the limits  $f_1$  and  $\infty$ .

A system of an infinite number of coupled circuits has an infinite number of degrees of freedom and has accordingly an infinite number of free periods of oscillations and will therefore be in resonance for impressed electromotive forces of frequencies corresponding to the free periods of the system. If the free periods of the system are limited to a finite range as given in the case above by the conditions of equations (20), the frequencies corresponding to the free periods of the system are close together, and we have the condition of band tuning. For a limited number of circuits the resonance frequencies are closer or farther apart, depending on the number of circuits, and the condition of band tuning is approximated if an appreciable number of circuits is

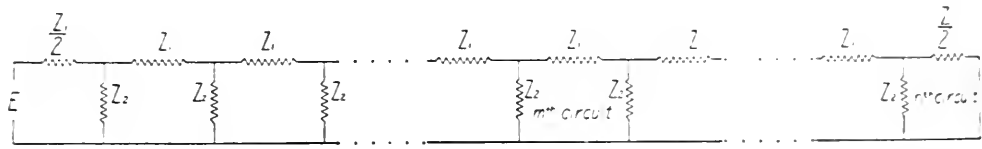


used. The electric filter is nothing more, of course, than a system of coupled circuits; the character of the coupling is immaterial, and should be considered as such. It is believed that looked at from the standpoint of coupled circuits, the physical interpretation of the operation of the electric filter is immediately obvious, and the explanation of its properties much simplified.

DIRECT COUPLED SYSTEM.

The general principles discussed above in connection with an electromagnetic coupled network of circuits are applicable to any system of circuits irrespective of the type of coupling adapted. The following is a brief discussion of a direct coupled system.

FIG. 2.



shown in Fig. 2, which is the most common arrangement used in the design of electric filter circuits.

The formulas are much simplified if the series reactances of the two end circuits are each assumed one-half the series reactance of any intermediate circuit.

The electromotive forces acting in each of the circuits except the end circuits is given by the following equation:

$$Z_1 I_m + Z_2 I_m - Z_2 I_{m+1} - Z_2 I_{m-1} + Z_2 I_m = 0,$$

or

$$(Z_1 + 2Z_2) I_m - Z_2 I_{m+1} - Z_2 I_{m-1} = 0. \tag{31}$$

For the two end circuits, the first and *n*th circuit, we have

$$\left. \begin{aligned} \frac{1}{2} Z_1 I_1 + Z_2 I_1 - Z_2 I_2 &= E \epsilon^{j\omega t}, \\ \frac{1}{2} Z_1 I_n - Z_2 I_{n-1} + Z_2 I_{n+1} &= 0. \end{aligned} \right\} \tag{32}$$

The solution of equation (31) is

$$I_m = A \epsilon^{m\gamma} + B \epsilon^{-m\gamma}, \tag{33}$$

which yields the relation

$$\epsilon^\gamma + \epsilon^{-\gamma} = 2 + \frac{Z_1}{Z_2},$$

or

$$\cosh \gamma = 1 + \frac{1}{2} \frac{Z_1}{Z_2}. \tag{34}$$



The constants  $A$  and  $B$  are determined from equations (32) by substituting the values of  $I_m$  from (33), which gives the following

$$\left. \begin{aligned} \left( \frac{1}{2} Z_1 + Z_2 \right) (A \epsilon^\gamma + B \epsilon^{-\gamma}) - Z_2 (A \epsilon^{2\gamma} + B \epsilon^{-2\gamma}) &= E \epsilon^{j\omega t}, \\ \left( \frac{1}{2} Z_1 + Z_2 \right) (A \epsilon^{n\gamma} + B \epsilon^{-n\gamma}) - Z_2 (A \epsilon^{(n-1)\gamma} + B \epsilon^{-(n-1)\gamma}) &= 0. \end{aligned} \right\} \quad (35)$$

Rearranging, the above simplify as follows:

$$\left. \begin{aligned} A \epsilon^\gamma + B \epsilon^{-\gamma} &= \frac{-2 E \epsilon^{j\omega t}}{Z_2 (\epsilon^\gamma - \epsilon^{-\gamma})}, \\ A \epsilon^{n\gamma} + B \epsilon^{-n\gamma} &= 0. \end{aligned} \right\} \quad (36)$$

The constants  $A$  and  $B$  are readily determined from the above two equations

$$\left. \begin{aligned} A &= \frac{2 E \epsilon^{j\omega t} \epsilon^{-n\gamma}}{Z_2 (\epsilon^\gamma - \epsilon^{-\gamma}) (\epsilon^{(n-1)\gamma} - \epsilon^{-(n-1)\gamma})}, \\ B &= \frac{2 E \epsilon^{j\omega t} \epsilon^{n\gamma}}{Z_2 (\epsilon^\gamma - \epsilon^{-\gamma}) (\epsilon^{(n-1)\gamma} - \epsilon^{-(n-1)\gamma})}. \end{aligned} \right\} \quad (37)$$

Substituting these values in (33), we finally get the expression for the current in any circuit

$$I_m = \frac{2 E \epsilon^{j\omega t} \{ \epsilon^{(n-m)\gamma} + \epsilon^{-(n-m)\gamma} \}}{Z_2 (\epsilon^\gamma - \epsilon^{-\gamma}) (\epsilon^{(n-1)\gamma} - \epsilon^{-(n-1)\gamma})}. \quad (38)$$

$$I_m = \frac{E \epsilon^{j\omega t} \cosh (n-m) \gamma}{Z_2 \sinh \gamma \sinh (n-1) \gamma}. \quad (39)$$

For the last circuit,  $m = n$ ,

$$I_n = \frac{E \epsilon^{j\omega t}}{Z_2 \sinh \gamma \sinh (n-1) \gamma}. \quad (40)$$

The current is of maximum value, the system is in resonance when the reactance part of the denominator in equation (40) vanishes. Neglecting the resistance of the circuits, the resonance condition is

$$\sinh (n-1) \gamma = 0, \quad (41)$$

and

$$(n-1)\gamma = js\pi, \quad s = 0, 1, 2, 3, \dots, n-1. \quad (42)$$

For values of  $s > n-1$  we get only a repetition of the values corresponding to  $s$  between 0 and  $n-1$ , and no new terms added.



To determine the frequencies which correspond to the values of  $\gamma$  given by (42) for any system of circuits, we use equation (34),

$$\cosh \gamma = 1 + \frac{1}{2} \frac{Z_1}{Z_2},$$

or

$$\cos \frac{s\pi}{n-1} = 1 + \frac{1}{2} \frac{Z_1}{Z_2} \quad (43)$$

Different inductance capacity arrangements in the series and shunt reactances  $Z_1$  and  $Z_2$  will give different results. By way of illustration we shall consider here several simple cases:

Case I. Inductance in series branch, capacity in shunt branch.

$$\begin{aligned} Z_1 &= Lj\omega, \quad Z_2 = \frac{1}{Cj\omega}, \\ \cos \frac{s\pi}{n-1} &= 1 - \frac{1}{2} LC\omega^2, \\ \omega^2 &= \frac{2 \left( 1 - \cos \frac{s\pi}{n-1} \right)}{LC}. \end{aligned} \quad (44)$$

For two sections,  $n = 2$ ,

$$\begin{aligned} \omega_1 &= 0, \\ \omega_2 &= \frac{2}{\sqrt{LC}} \end{aligned}$$

For three sections,  $n = 3$ ,

$$\omega_1 = 0, \quad \omega_2 = \frac{\sqrt{2}}{\sqrt{LC}}, \quad \omega_3 = \frac{2}{\sqrt{LC}}.$$

For four sections,  $n = 4$ ,

$$\begin{aligned} \omega_1 &= 0, \quad \omega_2 = \frac{1}{\sqrt{LC}}, \\ \omega_3 &= \frac{\sqrt{3}}{\sqrt{LC}}, \quad \omega_4 = \frac{2}{\sqrt{LC}}. \end{aligned}$$

As the number of sections is increased, the number of frequencies for which the system is in resonance is correspondingly increased; all the frequencies, however, being within the same frequency limits  $f_1 = 0$  and  $f_n = \frac{2}{\pi\sqrt{LC}}$ . For an infinite number of sections the system is in resonance for an infinite number of frequencies within a limited band of frequencies, which in the above case would be for all frequencies below the frequency

$$f_n = \frac{1}{\pi\sqrt{LC}}.$$



Case II. Capacity in series branch, inductance in shunt branch.

$$Z_1 = \frac{1}{Cj\omega}, \quad Z_2 = Lj\omega,$$

we have by (43)

$$\omega^2 = \frac{1}{2LC \left( 1 - \cos \frac{s\pi}{n-1} \right)} \quad (45)$$

For two sections,  $n = 2$ ,

$$\omega_1 = \infty, \\ \omega_2 = \frac{1}{2\sqrt{LC}}.$$

For three sections,  $n = 3$ ,

$$\omega_1 = \infty, \quad \omega_2 = \frac{1}{\sqrt{2LC}}, \quad \omega_3 = \frac{1}{2\sqrt{LC}}.$$

For four sections,  $n = 4$ ,

$$\omega_1 = \infty, \quad \omega_2 = \frac{1}{\sqrt{LC}}, \quad \omega_3 = \frac{1}{\sqrt{3LC}}, \quad \omega_4 = \frac{1}{2\sqrt{LC}}.$$

For an infinite number of sections, the system is in resonance for an infinite number of frequencies, that is, for all frequencies above the frequency  $f = \frac{1}{4\pi\sqrt{LC}}$ . The limiting frequencies for which the system is in resonance are the same in all cases irrespective of the number of sections used.

Case III. Series inductance-capacity in series branches, parallel inductance-capacity in shunt branches.

$$Z_1 = L_1j\omega + \frac{1}{C_1j\omega} = L_1j\omega \left( 1 - \frac{1}{L_1C_1\omega^2} \right), \\ Z_2 = \frac{L_2j\omega}{1 - L_2C_2\omega^2}.$$

For

$$L_1 = L_2, \quad C_1 = C_2, \\ \frac{Z_1}{Z_2} = \frac{2LC\omega^2 - L^2C^2\omega^4 - 1}{LC\omega^2}.$$

Substituting the above in (43), we get

$$\cos \frac{s\pi}{n-1} = \frac{4LC\omega^2 - L^2C^2\omega^4 - 1}{2LC\omega^2},$$

and

$$\omega^2 = \frac{2 - \cos \frac{s\pi}{n-1} \pm \sqrt{\left( 2 - \cos \frac{s\pi}{n-1} \right)^2 - 1}}{LC}. \quad (46)$$



For two sections,  $n = 2$ ,

$$\omega_1 = \frac{1}{\sqrt{LC}},$$

$$\omega_2 = \sqrt{\frac{3 \pm \sqrt{8}}{LC}}.$$

For three sections,  $n = 3$ ,

$$\omega_1 = \frac{1}{\sqrt{LC}},$$

$$\omega_2 = \frac{\sqrt{2 \pm \sqrt{3}}}{\sqrt{LC}},$$

$$\omega_3 = \frac{\sqrt{3 \pm \sqrt{8}}}{\sqrt{LC}}. \quad (46)$$

For four sections,  $n = 4$ ,

$$\omega_1 = \frac{1}{\sqrt{LC}}, \quad \omega_2 = \frac{\sqrt{\frac{1}{2}(3 \pm \sqrt{5})}}{\sqrt{LC}}$$

$$\omega_3 = \frac{\sqrt{\frac{1}{2}(5 \pm \sqrt{21})}}{\sqrt{LC}}, \quad \omega_4 = \frac{\sqrt{3 \pm \sqrt{8}}}{\sqrt{LC}}.$$

For an infinite number of sections the system is in resonance for an infinite number of frequencies, the extreme limits of which are  $f_1 = \frac{1}{2\pi} \sqrt{\frac{3-\sqrt{8}}{LC}}$  and  $f_n = \frac{1}{2\pi} \sqrt{\frac{3+\sqrt{8}}{LC}}$ , all the frequencies between these limits pass freely. It is to be noted that in this case because each section consists of an inductance capacity in the series branch and an inductance capacity in the parallel branch, each section is in itself a double periodic system, and hence for  $n$  sections the system is in resonance for  $2n$  frequencies. If  $Z_1 \neq Z_2$  the system is in resonance for two distinct and separate bands of frequencies. By making  $Z_1 = Z_2$ , as we have done in the above case, the two frequency bands coalesce and one frequency is common to the two bands of frequencies. The number of frequencies for which the system is in resonance is reduced by one, that is, for  $n$  sections the resonance frequencies of the system are  $2n - 1$ . In this case the frequency  $f = \frac{1}{2\pi\sqrt{LC}}$  is the common frequency of the two bands.



It is evident from the above considerations that no matter what type of circuit connections is used in electric filter circuits, it is in all cases the equivalent of a system of coupled circuits. The system is in resonance for a number of frequencies, within the frequency limits determined by the electrical constants of the circuits, corresponding to the number of individual circuits used. The ideal condition of band frequency tuning can be realized only with an infinite number of circuits, but this condition is approximated even when only a limited number of circuits is used.

---

**The Effect of Temperature on Gravitative Attraction.** P. E. SHAW and N. DAVY. (*Proc. Royal Soc.*, A 714.)—"Previous work by one of us with a torsion balance of the Boys-Cavendish type had appeared to indicate that the so-called Newtonian Constant of Gravitation increases slightly as the attracting bodies are heated. The attempt has now been made to carry the work to a higher order of accuracy with a view to confirming or disproving that result. The clearing up of this point has become of greater importance on account of the recent development in the theories of gravitation." The greatest care was exercised to exclude tremors originating in distant trains from the apparatus. This having been accomplished, an elevation of temperature from  $0^{\circ}$  to  $250^{\circ}$  made no change in the value of the gravitational constant. The authors are of the opinion that "slight displacements of the heavy masses occurring during the experiments introduced systematic errors in the former work."

G. F. S.

**On the Susceptibility of Feebly Magnetic Bodies as Affected by Compression.** ERNEST WILSON. (*Proc. Royal Soc.*, A 712.)—This investigation may "possibly throw some light upon the susceptibility of the earth's crust as affected by the enormous forces with which it has to contend, and their variations." The stresses applied were all compressive and extended to about 1200 kilograms per square centimetre.

The susceptibility was measured at right angles to the stress and also along it. In the former direction some small increases were noted as the stress increased. In the case of a dolerite the increase was as much as 10 per cent., while no change at all was found in the specimen of New York magnetite which manifested the largest change in longitudinal susceptibility. This property for this particular ore of iron diminished to half of its initial value upon the application of pressure. Other magnetites from Arkansas and Manchuria showed an effect in the same direction but to a very small degree.

G. F. S.



## AN IMAGINARY THERMODYNAMIC PROCESS.\*

BY

JOSEPH S. AMES, Ph.D., LL.D.

Director, Physical Laboratory, Johns Hopkins University, Baltimore, Maryland,  
Associate Editor, Member of the Institute.

IN presenting to students the concept of entropy and in emphasizing the essential steps in the logical development of the subject, great difficulties are encountered, as every teacher knows, owing to the refusal on the part of most men's minds to appreciate the meaning of things about which their senses give them no information. Strange to say, students accept without a qualm such words as "energy," "electricity," "unit pole of magnetism," etc., and yet draw back in alarm from "entropy." They seem to require a picture, and do not hesitate to supply their own; for entropy they have none.

I have found that a somewhat similar problem to that of the Carnot-Clausius one could be developed in such a manner as often to help a student to overcome his reluctance to adopt the concept of entropy. Just why this is so, I do not know.

In the proof of the existence of a property which is called entropy, the method usually followed is to consider two Carnot engines, whose operation is described on a pressure-volume diagram by means of isothermals and adiabatics. If an analysis is made of the instruments and fundamental concepts required, it will be found to include the following:

- (1) Concept of a substance all of whose properties are defined by a knowledge of two, *e.g.*, pressure and volume.
- (2) Instruments to measure pressure and volume.
- (3) A thermoscope to indicate when the temperature of a body is kept constant and if two bodies have different temperatures. (There is no need of having a temperature scale.)
- (4) A knowledge of what is meant by work done by mechanical forces, *e.g.*, in the case of an expanding fluid,  $\Delta W = pdV$ .
- (5) A means of measuring heat-quantities, *i.e.*, the amount of energy transmitted by the processes of radiation and conduction.
- (6) Two "baths," or reservoirs, of infinite heat capacity.

---

\* Communicated by the Author.



(7) Apparatus for varying the pressure between certain limits by a series of infinitesimal steps, *e.g.*, by use of weights.

Then isothermal and adiabatic processes may be described; the corresponding curves on a pressure-volume diagram, for any fluid, may be drawn; the conditions for a process to be performed in a reversible manner may be specified; the measurement of amounts of heat and work may be assumed possible; the first and second principles of thermodynamics will be accepted by any student; and so he is led to a definition of an "absolute." scale of temperature and to the proof of the existence of a new definite property of a body, for which the absolute value is not known, but whose changes may be measured (like potential energy). The student, as a rule, finds no difficulty till the very end. He knows—or thinks he does—about force and area, and therefore pressure; he can see that a body occupies space, so volume offers no difficulty; he has a temperature sense; he has been taught about heat, and energy, heat-engines, etc.

Now, let us assume the existence of a being who has no knowledge of space or of space measurements—but let him have sense-organs for temperature, entropy and force, and instruments for giving numbers to them; let him be able to measure the transfer of energy both by mechanical processes and by thermal processes, knowing, moreover, that, if  $\Delta H$  is a small amount of heat added to a body temperature at  $T$ , and if  $S$  is its entropy,  $\Delta H = TdS$  provided the proper scale of temperature is adopted. By experimenting with a tank containing some gas, which is fitted with various pistons, he could be conscious—by his force sense—of the outward thrust of the gas and of the fact that the different pistons require in general different balancing forces in order to keep them at rest. By studying various physical properties of bodies, *e.g.*, the electrical resistance of a wire, he may learn that this remains the same wherever the wire is located in the tank, but that it is different, in general, if it is placed in a gas contained in a different tank. The numerical value of this resistance may be taken to measure that property of the gas which produces the outward thrust—call this property, for convenience, "pressure." If there are two tanks, each fitted with a single piston, the two pistons being connected by a rod perpendicular to their faces, the action of the gas in one tank upon that in the other may be studied. Even if the pressure in each gas, as tested by means of



the resistance method, is the same, it will be observed that the connecting rod will, in general, be pushed one way or the other; but, by trying different pistons, two may be found such that, if they are used in the case when the two gases are at the same pressure, the double piston will not move. Then, if the pressure in one of the tanks is changed, as determined by the resistance method, the double piston will move.

(It is assumed, of course, that in the use of the resistance method care is taken to avoid temperature effects. It is also obvious that by a choice of two "standard pressure conditions" and by arbitrarily assigning numbers where necessary, a scale of

pressure can be defined by  $p = p_1 + \frac{r - r_1}{r_2 - r_1}$ , corresponding to the ordinary definition of a temperature scale.)

The equipment of this imaginary being would then be as follows:

(1) Concept of a substance all of whose properties are defined by a knowledge of two, *e.g.*, temperature and entropy.

(2) Instruments to measure temperature on what is called the absolute scale and changes in entropy. (By assigning a number to the entropy in some standard condition, the values for any other condition would be known.)

(3) An instrument to indicate when the "pressure" of a fluid is kept constant, and if two fluids have different pressures. (There is no need of having a pressure scale.)

(4) A knowledge of what is meant by adding or withdrawing heat, *e.g.*, that  $\Delta H = TdS$ .

(5) A means of measuring mechanical work.

(6) Two large tanks, so large that for small displacements of their pistons there is no change in "pressure."

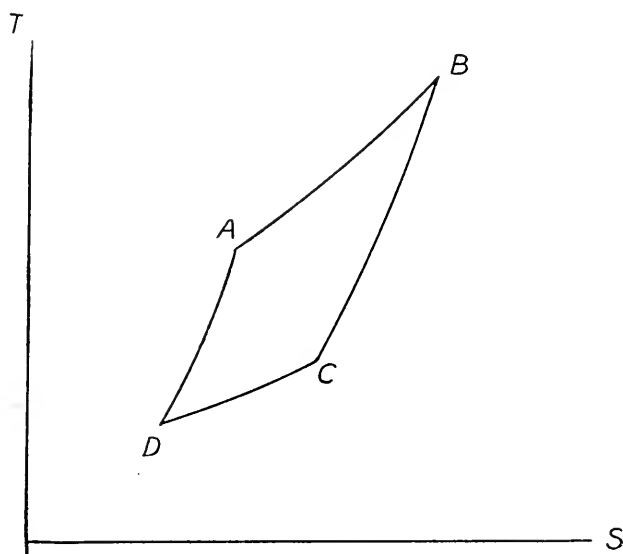
(7) Apparatus for varying the temperature between certain limits by a series of infinitesimal steps, *i.e.*, a series of thermal baths.

Let there be a gas container fitted with a double piston, as described above, the other piston fitting into another large tank such as specified in (6) above; let each tank be provided with resistance coils and let conditions be adjusted until the "pressure" in both gases is the same. Let the temperature of the "working substance," *i.e.*, the gas in the container, be  $T$  and its entropy  $S$ ,



the container being surrounded by a bath at the same temperature. It is a condition of mechanical and thermal equilibrium, and can be described by a point  $A$  on a temperature-entropy diagram. By adding small quantities of heat to the gas in the container, by placing the container in a thermal bath at temperature  $T + dT$ , etc., its temperature and entropy will both increase gradually, while its "pressure" remains unchanged, owing to its connection with the large tank. In this manner an "isobar,"  $AB$ , may be described by the gas in the container. The process will be reversible if each point of the curve represents a condition of equilibrium, that is,

FIG. I.



Elementary cycle on temperature-entropy diagram.

if the experimenter has at his disposal a series of "baths" with which to surround the container, whose temperatures vary by infinitesimal steps from  $T_A$  to  $T_B$ . In the process the amount of heat withdrawn from the baths and added to the gas is  $\int TdS$ , or the area between the curve and the axis of entropy; and a certain amount of work  $W_1$  has been done on the gas contained in the large tank, which may be called  $P_1$  tank. When the gas has reached a certain state described by the coördinates of  $B$ , let the piston of the gas container be clamped. Then, by a series of steps, heat may be withdrawn from the gas, until its temperature and entropy are lowered to the corresponding coördinates of a point  $C$ , the curve described being called an "argonic," because no



mechanical work is done. (The process may be made in a reversible manner if a series of suitable thermal baths are used.) The argonic is steeper than the isobar because in the former process when heat is added or subtracted all the energy is used for the change in temperature of the gas, and therefore a given change in entropy corresponds to a greater change in temperature. When the gas is in the condition  $C$ , its double piston may be fitted into a different large tank, which may be called  $P_2$ , so chosen that its "pressure" is the same as that of the gas itself in the condition  $C$ . The piston may now be unclamped; heat may be withdrawn from the gas—by a reversible process if desired—until the gas reaches a condition indicated by the coördinates of the point  $D$ . In this isobaric process heat is added to the baths, and the gas in the large tank  $P_2$  does a certain amount of work,  $W_2$ . When the condition  $D$  has been reached, the piston may be again clamped; and if heat is added to the gas by infinitesimal steps, an argonic will be described. If the "stroke"  $CD$  is suitably chosen, this argonic will pass through the initial point  $A$ . A cycle will have been described by the working substance, the gas in the container. In the cycle the net amount of heat withdrawn from the baths and added to the gas is  $H = \int TdS$  around the cycle, *i.e.*, it equals the area of the cycle on the diagram. The gas in tank  $P_1$  has had an amount of work done on it equal to  $W_1$ , and that in tank  $P_2$  has done an amount of work  $W_2$ . Therefore, by the conservation of energy

$$H + W_2 = W_1$$

or

$$H = W_1 - W_2$$

Similarly, another gas container, with a different gas, may be made to describe a cycle making use of the *same* two tanks  $P_1$  and  $P_2$ . Let the amounts of heat and work involved be called  $H'$ ,  $W'_1$  and  $W'_2$ . Then,

$$H' = W'_1 - W'_2$$

It has been noted that all the processes involved in the two cycles may be performed in a reversible manner; so, if the first cycle is reversed, the net result is that the net heat added to the



baths, being withdrawn from the gas, is  $H$ ; the gas in tank  $P_1$  does work  $W_1$ , and the gas in tank  $P_2$  has work  $W_2$  done on it. Therefore

$$W_1 = W_2 + H$$

or, of course,

$$H = W_1 - W_2$$

If the "strokes" of the two cycles are chosen suitably, their areas may be made the same; so the net amounts of heat involved in the two cycles are the same, *i.e.*,  $H = H'$ . Then, if the first cycle is performed in a reverse sense, and the second cycle in a direct sense, the net result is that the gas in tank  $P_1$  has done an amount of work  $W_1 - W'_1$  and that in tank  $P_2$  has received an equal amount of energy  $W_2 - W'_2$ . In performing the various steps in the two cycles, heat has been added or taken from various thermal baths and therefore their entropies have been changed; but, since the net amount of heat  $H'$  added to the working substance in the second cycle equals the net amount of heat  $H$  taken away from the working substance in the first cycle when reversed, there are quantities of heat available which may be taken from or added to the thermal baths, so as to restore them to their former entropies. By processes of radiation this restoration would result in leaving the hottest bath used in a condition of having lost an amount of heat, and the coldest bath used in a condition of having added to it an equal amount. To complete the restoration, our imaginary being must be able to reverse this, *i.e.*, to take away heat from the cold bath and add it to the hot one, *without doing any mechanical work*. This power, then, is assumed; it is not contrary to the conservation of energy. (Compare, Maxwell's "demon.") Consequently at the end of the combined cyclical processes, cycle one reversed and cycle two direct, the only changes in the whole "apparatus" are: Gas in tank  $P_1$  has done an amount of work  $W_1 - W'_1$ ; gas in tank  $P_2$  has had done upon it an equal amount of work  $W_2 - W'_2$ .

Experience with two tanks containing gases at different "pressures" would convince the observer that, if one is allowed to do work upon the other, connecting them by means of a double piston, the result is always in a definite direction. That is, if  $R_1$  is the electrical resistance of the "pressure indicator" when placed in one tank; and, if  $R_2$  is its resistance when placed in the other, experiments will show that, if  $R_1 = R_2$ , no work is done, and that,



if  $R_1 \neq R_2$  in all cases work is done by the tank for which  $R$  is the greater, or for which  $R$  is the less. Experiments will decide which of these two is correct—it will depend upon the type of pressure indicator selected; but the result is always definite and unidirectional. The tank which *does the work* is said to have the “higher pressure.” Other experiments will show that, if a gas is in a container whose piston is clamped, and, if heat is added to it, the “pressure” is thereby increased. This proves that in the case of the cyclical processes discussed previously the pressure in tank  $P_1$  is higher than in the tank  $P_2$ .

The experiments just referred to may be described by saying that, if there are two tanks at different pressures and if the only change taking place in nature consists in the gas in one tank doing work and in work being done on the gas in the other, the gas in the tank at the higher pressure is the one that does the work. In other words, if there are two pressure tanks at different pressures, the gas at low pressure cannot do work upon the other, provided there are no other changes in the system. In the case of the combination of the two cycles previously described, the gas in tank  $P_1$ , the one having the higher pressure, does the work  $W_1 - W'_1$ ; and, therefore, in accordance with this principle, this cannot be a negative quantity; hence

$$W_1 - W'_1 \geq 0$$

Similarly, if the first cycle is performed in a direct manner, and the second in a reverse one, the work done by the gas in the tank at the higher pressure is  $W'_1 - W_1$ , and hence

$$W'_1 - W_1 \geq 0$$

It follows, then, that  $W_1 = W'_1$ , when  $H$  is made equal to  $H'$ ; and therefore the ratios  $\frac{H}{W_1}$  and  $\frac{H'_2}{W'_1}$  are the same, regardless of the working substance used or of the length of the stroke, for all cycles made up of reversible isobaric and argonic processes, use being made of the same two pressure tanks  $P_1$  and  $P_2$ .

[This same theorem may be deduced in a different manner. Let the stroke of the two cycles be adjusted until  $W_2 = W'_2$ . Then, if the first cycle is reversed and combined with the second performed directly, the net result is that the mechanical work done



is by the gas in tank  $P_1$  alone, being  $W_1 - W'_1$ , and that an equivalent amount of heat  $H_1 - H'_1$  has been added to the thermal baths involved in performing the two cycles. Our imaginary being would find as a fact of experiment that, when the only changes in nature are processes by which the pressure in a single pressure tank is changed and heat is added to and taken from certain bodies, the process is always unidirectional, in the sense that the mechanical work done by the tank cannot be a positive quantity, *i.e.*, he has no way by which he can obtain mechanical work from a gas in a pressure tank except by letting it do work on another pressure tank. Then, in the case of the combination of the two cycles just described,  $W_1 - W'_1 \leq 0$ . Similarly, if the combination of cycles is reversed,  $W'_1 - W_1 \leq 0$ ; and, therefore,  $W_1 = W'_1$ . Since  $W_2$  was made to equal  $W'_2$ ,  $H = H'$ , etc.]

Since the ratio  $\frac{W_2}{W_1}$  depends only upon the pressure conditions in the two tanks; that is, since the numerical value of this ratio as determined by the use of any working substance is independent of this substance, it is obvious that the proper way of assigning numbers to the pressure in the two tanks is to select two such numbers  $p_2$  and  $p_1$ , as will make

$$\frac{p_2}{p_1} = \frac{W_2}{W_1}$$

If some standard pressure condition is adopted and if a definite number is assigned to this, then the number for the pressure of any other condition (*e.g.*, in a pressure tank) is definite.

Using this "absolute" scale of pressure, a simple cycle on the  $T$ - $S$  diagram is described by the equation

$$\frac{W_1}{p_1} = \frac{W_2}{p_2}$$

in which  $W$  is the mechanical work done by (or upon) the working substance while it is at a pressure  $p$ .

In any one of the original cycles, consisting of two isobars and two argonics, the  $\int \frac{\Delta W}{p}$  around the cycle equals  $\frac{W_1}{p_1} - \frac{W_2}{p_2}$  and therefore is zero. Any cycle on the temperature-entropy diagram can be regarded as the summation of a number of such elementary cycles; and, since  $\int \frac{\Delta W}{p}$  around a cycle equals zero, there must be



a "property" of the working substance such that, calling its numerical value by the symbol  $V$ ,

$$\frac{\Delta W}{p} = dV$$

*i.e.*, the work done by the substance while this property is increasing by an amount  $dV$ , its pressure being  $p$ , is given by  $\Delta W = p dV$ . This new property, whose "existence" is deduced from indirect observations, may be called "volume."

It is obvious that all that is given by the equation of definition is a knowledge of  $dV$ , *i.e.*, the change in volume. To obtain a value for the volume itself,  $V$ , it is necessary to assign a number  $V_0$  to the volume of the substance under some standard condition

of temperature and entropy, and then  $V = V_0 + \int_0 \frac{\Delta W}{p}$ , where the integral is taken along a "reversible path." (Of course the actual value of  $V$  in any condition does not depend upon the use of reversible processes to reach it; but, if one wishes to know the value, it is necessary to use them.)

---

**An Experimental Investigation of the Dispersion of a Limited Wave Train.** I. H. SOLT. (*Phys. Rev.*, December, 1922.)—When an electromagnetic wave passes from one medium to another certain things take place that are not in accord with the common conception of dispersion and refraction. "In the neighborhood of an absorption band the index of refraction of a dispersing medium may be less than unity and consequently the velocity with which a given wave crest in a monochromatic wave train is propagated may exceed its velocity in a vacuum. This is true only after the medium has reached a steady state, *i.e.*, theoretically, for an infinite wave train. From this one might conclude that a signal could be sent with a velocity greater than the velocity of light in vacuum in contradiction to the principle of relativity." According to the theory elaborated by Sommerfeld, Brillouin and Colby, when a ray falls upon a dispersing prism, at the very earliest stage of transmission the wave front goes through with vacuum velocity and without deviation at the boundaries. "As time goes on the disturbance in the medium swings continuously toward the normal until the steady state is reached when it has the direction required by the ordinary law of refraction. The period of the first part of the disturbance is very short and the amplitude very small. Both quantities decrease with increasing obliquity, and increase as time goes on, the latter passing through a maximum and minimum before the steady state is reached."



This investigation deals with these evanescent phenomena occurring before the steady state is established. The source of energy was a Righi vibrator consisting of two steel balls actuated by two type P pliotrons in parallel giving a frequency of 170,000. The wave from the vibrator fell upon a pitch prism with a refracting angle of  $30^\circ$  and with faces 75 cm. high by 85 cm. long. The receiver of the transmitted energy was a crystal detector. "Since the effect we are investigating is very small and associated only with the beginning of a wave train, it is essential to use a source of radiation which emits a very large number of short wave trains per second. . . . The most convenient type of radiation to use is the highly damped wave emitted by the Righi vibrator. In this case most of the energy will be in the first period and hence the effect we are looking for will be a larger proportion of the total energy than would be the case if a longer wave train were used."

The prism was fixed. Then the receiver was moved along the arc of a circle described about a point in the axis around which the prism turned. The energy received at different positions along the arc was measured. When the ray fell on the face of the prism at right angles (angle of incidence  $0^\circ$ ) the energy that came straight through the prism was 26 per cent. of the maximum energy found for all positions examined. As the angle of incidence was made smaller the relative proportion of the energy directly transmitted became less, as theory predicted. For an angle of incidence equal to  $35^\circ$  it was only 8 per cent. of the maximum amount. Upon moving the receiver from its position in the prolongation of the incident ray toward the normally refracted ray it recorded a greater and greater amount of energy received. A maximum was reached and, of course, beyond this the energy diminished. The minimum angle of deviation for all such maxima was  $32^\circ$ , from which the index of refraction of pitch is calculated to be 1.99. This is for waves 7.8 cm. Hertz found the index to be 1.67 for waves of length 60 cm. G. F. S.

**New Lead Mineral.** SAMUEL G. GORDON (*Proc. Acad. Nat. Sciences*, 1922, 74, 101-103) describes keeleyite, a new lead mineral from the San José mine, Oruro, Bolivia. It is dark gray with a bright metallic lustre, has a specific gravity of 5.21, and occurs in crystalline aggregates which are probably orthorhombic. Keeleyite is a lead sulphantimonite (thioantimonite), and has the formula  $\text{Pb}_2\text{Sb}_2\text{O}_{11}$  or  $2\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$ . J. S. H.

**Rubber-lined Steel Tanks.** F. C. ZEISBERG (*J. Ind. Eng. Chem.*, 1923, 15, 157-158) describes a steel tank which is lined with a layer of soft rubber, then a layer of hard rubber. The lining is vulcanized in position under considerable pressure. Tanks of this construction have been placed on flat cars and used for the transportation of hydrochloric acid. They may be used for the transportation of any liquid which does not attack the inner lining of hard rubber.

J. S. H.



## HIGH TEMPERATURE INVESTIGATION.\*

BY

EDWIN FITCH NORTHRUP, Ph.D.

Member of the Institute.

I. Up to the close of the last century science has been almost wholly occupied in a study of the properties of matter and the phenomena of energy transformations as these exist under the relatively quiescent conditions which maintain in the environment of the observers. The body of physical and chemical science has developed in nature's doldrum. Only recently have artificial means and special contrivances been employed to subject matter to the action of forces of greater magnitude, to cause energy transformations of greater rapidity, and to produce temperature variations of greater degree than occur in phenomena of natural production at the surface of the earth. The laws of physics were slowly, painfully, but progressively established from accumulated observations in laboratories to which profound reasoning and mathematical analysis were applied. The observations, however, were confined to densities, velocities, electric potentials, magneto-motive forces, temperatures, etc., easily producible without special contrivances in the restricted surroundings of the observers. The variables were varied under controlled conditions through ranges which are small indeed when compared with their possible extent as revealed by modern astrophysics. The functions of these variables, changed through narrow limits, were determined by accurate observation and brilliant deduction. Curves to express these functions were drawn for the limits of the observed variations, and the laws of physics in these limited ranges were firmly established. But imagination has too often gone hand-in-hand with experimentation. With but a trifling percentage established by observation of the long curves relating functions and variables that nature knows, scientists have dared to speculate, and formulate equations which they intend shall correctly express the entire courses of these curves. But beyond the range of observation, the

---

\* Presented at a meeting of the Section of Physics and Chemistry held Thursday, March 1, 1923.



true plan of nature is not revealed. The "plan of nature," when mapped out by extrapolations of short length curves drawn through points of observation, is of necessity an imaginary chart. Such extrapolations have, doubtless, a psychic value spurring research to well-directed effort, but the attitude of true science will be agnostic for all that lies in the region of pure surmise which bounds the area of actual observation.

The "new science" of physics which began to make itself strongly felt in the beginning of this century, had its inception in no changed attitude of men's minds as had the rapid advance of science in the period of the Renaissance. Then metaphysics gave place to science, and Aristotle ceased to dominate thought because there came, as it were, a gift from heaven in the form of a desire on the part of men to learn about nature through controlled observation. Francis Bacon formulated in a speculative way the new scientific method, but it was Gilbert, the father of magnetism, who first put it into effect, and reported in 1600 his successes in his classic "*De Magnete*." The science of nature as observed in our dwelling place, the earth, made an advance comparable to the butterfly in emerging from its chrysalis. The Newtonian laws of mechanics were firmly established for slow motions; the wave theory of light was proved—for a narrow range of wavelengths; the electrical and magnetic properties of bodies were observed, and the laws of electricity and magnetism were rapidly formulated—for low potentials, small magnetomotive forces and where matter in the mass was under consideration; the general nature of heat, the laws of heat flow and a proper conception of temperature and its effects on matter were firmly established—for a little degree of heat concentration and a trifling range of temperature; the mechanical equivalent of heat was accurately ascertained for work expended on matter—in the mass.

With the beginning of the twentieth century there began another period of rapid advance in scientific knowledge—but of a different character. Explorations began into regions where matter exists under conditions far different than those which naturally maintain in man's abode. The constitution of matter began to be studied under circumstances exceptional on this planet and the door was opened to startling revelations.

There was no change, however, in the attitude of men's minds. The firmly rooted scientific method continued to be used. But if



the startling advance of the last two decades is not due to a changed method or to a new attitude of mind, whence came it? The answer plainly is, that our modern new science wherein the constitution and laws of matter throughout the cognizable universe are investigated, is chiefly due to and dependent upon the invention and widening use of new and powerful tools, or instruments of research, which enable us to subject matter on earth to conditions which maintain naturally only in the skies.

When in 1892 Moissan presented to the Academy of Science his first model of an electric furnace consisting of a powerful arc housed in a chamber of quicklime, he at one bound carried inorganic chemistry into a sphere before only known in the sun's chromosphere. In his furnace which would melt tungsten he learned that every specific property of matter familiar in the range from  $0^{\circ}$  to  $100^{\circ}$  C. of temperature, which the exponents of thermotics had so thoroughly investigated, disappeared or became profoundly modified.

Inventions followed rapidly of other instruments of research with which the investigator can submit portions of matter, here on earth, to many of the conditions which are supposed to exist far below the earth's crust or in the extra mundane world. Testing machines were built to tear asunder large sections of the most tenacious steel. Pressure apparatus was devised which will squeeze a portion of matter with a pressure of 300,000 pounds per square inch, or about 20,000 atmospheres.<sup>1</sup> This is about ten times the explosion pressure in a large gun. The use of this apparatus has lead to many new observations on the properties of matter previously unsuspected. Yellow phosphorus, for example, becomes changed under high pressure to a brownish material of increased density and electrically conducting.

The invention of electromagnets, with which great field intensities can be produced, lead to the discovery of the Zeeman effect and to a method of measuring the ratio of the electric charge to the mass of an electron.<sup>2</sup>

The building of apparatus capable of supplying several kilowatts at a potential of a million volts has given a better understanding of the dielectric properties of air, the laws of corona formation, and the nature and behavior of insulators. The indus-

---

<sup>1</sup> T. W. Bridgman, *Science Abstracts*, Sec. A., No. 289, Jan. 31, 1922, p. 3.

<sup>2</sup> Kaye and Laby, "Phys. and Chem. Constants," p. 99.



trial value in power and voice transmission of this new knowledge is inestimable.

The invention of apparatus—the molecular vacuum pump—for extracting the last residues of gas from an evacuated space, has enabled investigators to determine the laws which govern electrons when wholly freed from matter. Perhaps no single apparatus has ever been devised with which a physical condition is carried to an extreme limit, that so profoundly affects life, as the highly evacuated electron tube.

The radioactive properties of matter appear to be independent of any physical and chemical conditions observed in nature or which can be produced in the laboratory. It is, together with gravitational attraction in this respect, unique. For its discovery no apparatus capable of producing extreme temperatures or forces was required. Nevertheless such apparatus is required to prove the lack of dependence of radioactivity upon physical and chemical forces.

In this brief survey we see that the advantages of studying the properties of matter, and transformations of energy under conditions produced artificially which approach those found in parts of the universe other than the surface of the earth are great indeed. These advantages come from a rapid increase in knowledge of the constitution of matter itself, and from an understanding of how to preserve for our uses some of the altered properties of matter brought about by extreme conditions, when normal conditions are restored. Materials which have been given permanently certain new properties often prove to be invaluable for the uses of everyday life. Thus, when silicon oxide in association with carbon is elevated to over  $2000^{\circ}$  C., silicon carbide (carborundum) is formed, and the new compound remains carborundum when the temperature is reduced to life temperature where the material with its new properties can be used in the industries.

II. Temperature is a condition under which all matter exists. It is the easiest condition to change artificially, and no change in a single condition affects to a greater extent the properties of a body. Indeed if the temperature is sufficiently raised only gravity and the radioactive properties of matter remain unaltered. Different kinds of matter when subjected for a time to high temperature have their properties permanently changed in widely different degrees. The pure elements are little affected



permanently; for when restored to the temperature from which they were raised the majority of their manifested properties and their familiar appearance return. The same is true of many very stable inorganic compounds, notably the pure oxides of the metals. Other inorganic compounds are readily disassociated by elevation of temperature and do not reassociate when the temperature is lowered. The organic non-living compounds are mostly broken down by moderate increase of temperature, and most living organic matter ends its life at about  $45^{\circ}$  C. Some organisms, *oscillaria*, have been reported by Morgan to live in hot springs in Iceland and at the extreme temperature for living matter of  $98^{\circ}$  C.<sup>3</sup>

A mere elevation of temperature if sufficient will so profoundly modify all the manifested properties of any portion of matter while at the elevated temperature, that it is difficult of recognition as the same thing. It is the retention only of the same mass, the same weight, and the same ratio of the chemical elements which it contains, by which its identity is at all recognizable.

To increase the temperature of a mass is to add to it a quantity of energy. But a mass may have its energy content increased in other ways without producing any marked physical or chemical change, as does increase of temperature. Thus, magnetizable matter is given an increase of energy content by magnetization. If the body is a dielectric it can be given an increment of energy content by electrification. All matter has its energy content increased by separating it from other matter, and all matter may become a storehouse of a considerably increased quantity of energy by imparting to it rapid motion, translatory, rotary, or both. Adding energy to a body in these ways does not, to any marked degree, affect its physical or chemical properties. But when we add energy to a body in the form of heat, thereby increasing its temperature, we always more or less profoundly change the body physically, and often chemically. Why this difference? Let us first consider a particular example. The answer will then become obvious.

Consider a steel sphere, such as is used for ball-bearings. Let us rotate this about a vertical diameter at a very high velocity. Conceivably the angular velocity of the sphere could be made very

---

<sup>3</sup> "Principles of Breeding," p. 311, by E. Davenport, published by Ginn and Co.



high by placing it in a rotary magnetic field and eliminating air friction by use of vacuum. A rotating field of almost any desired velocity of rotation could be produced by means of multiple circuits in which continuous oscillations differing in phase are maintained by means of electron tubes. By thus rotating the sphere it would be given an increment of energy. It is not to be supposed, however, that even with extremely high angular velocity imparted to the sphere, its normal properties as elasticity, density, magnetic permeability, color, etc., would be modified to any appreciable degree. The centrifugal stresses would deform it somewhat, but in all essentials it would remain the same familiar object when in rapid rotation as when at rest.

Now, with the sphere at rest, increase its temperature. Bring its increase in temperature to a point where the increase in the energy content in the form of heat of the sphere is exactly the same as was previously imparted to it in the form of kinetic energy of rotation. By this increase of energy content through increase of temperature, the properties of the steel become changed, very profoundly changed, if the temperature elevation is considerable.<sup>4</sup>

We readily find by calculation <sup>4</sup> that for a steel sphere 6 cm. in diameter, the relation holds,  $N = 287 \sqrt{T}$ . At a temperature of about 730° C. the steel has lost its magnetic permeability, its tensile strength, and many other familiar properties, and is a red-hot body. To give the sphere the same energy content by rotation, and change none of its physical or chemical properties, it would

---

<sup>4</sup>The revolutions  $N$  per second which the sphere must make for its content of kinetic energy of rotation to equal the increase in heat energy of the stationary sphere, due to a temperature rise  $T$  is calculated thus: Energy of rotation,

$$E_r = \frac{1}{2} I W^2 = 2\pi^2 I N^2 = 0.8\pi^3 m r^2 N^2$$

where  $I = 0.4 m r^2$  is the moment of inertia of the sphere about a diameter,  $m$ , the mass, and  $r$ , its radius.  $W$  is its angular velocity, and  $N$ , its revolutions per second.

The heat energy imparted to the sphere by a temperature rise  $T$  is  $E_h = JQ = JTms$ , where  $J = 4.2 \times 10^7$  ergs;  $m$  = the mass, and  $s$  = the specific heat of steel. Thus, equating these two expressions for energy content we obtain  $N^2 = \frac{J_s}{0.8\pi^2 r^2} T$ . If we call the specific heat  $s = 0.14$  and choose a sphere of radius 3 cm., we obtain finally  $N = 287 \sqrt{T}$ . Thus, if the sphere is raised in temperature 100° C. as much energy will be added to it as would be added by imparting to the sphere 2870 revolutions per second.



have to revolve 7749 revolutions per second. It might not be possible to impart so high an angular velocity even by means of a rotating magnetic field, but the conception of this brings out the principle to be noted, which is this: In the case where the energy content is due to rotation of the sphere all ultimate particles composing the sphere are moving uniformly in circles which have a common axis. The motions of all the particles are *organized* in the sense that all move in the same direction around a common axis with the same angular velocity. The relative spacing of the particles with reference to one another remains unchanged. There is, therefore, no jostling of particles one against another, and consequently no development of atomic or molecular vibrations.

In the other case where the stationary sphere is raised in temperature by receiving an increment of heat, it acquires energy. According to the best views of science it is kinetic energy, but the total kinetic energy so received is simply the sum of the kinetic energies of motion of the countless ultimate particles which compose its mass. But now we have these ultimate particles moving at any given instant in all possible directions and with widely varying velocities. The relative spacing between particles is every instant varying. Each particle crowds for more room, and the mass expands. The particles jostle one another, and internal vibrations of atoms and electrons are established which give forth electromagnetic radiations. If the body is brought into contact with another body in which motions of its particles are less active, the first body imparts some of the motion of its particles to the second body. In other words, heat flows from the body of higher temperature to the body of lower temperature. Now we note that the unique characteristic of heat motion of particles is that the motion of all the particles is highly *disorganized* motion. In the vicissitudes of any body played upon by the forces of its environment, the least probable motion for the mass to acquire is that of a uniform translation or a uniform rotation, and only by either one or both of these motions combined can all the ultimate particles of the body become marshalled into uniform organized motion. Thus of all forms of energy which may be imparted to a mass, that form is the most probable one which gives to its ultimate particles a highly disorganized motion. All organized motions by the law of probability tend to become disorganized motions, and so we see that all forms of energy imparted to



masses tend to assume finally the form of heat. But by heat energy chiefly are physical and chemical changes produced in matter. As this type of kinetic energy is the most probable type, we must conclude that by the very laws of chance matter is destined to assume its varied forms, aspects and endless properties.

We are thus led to view increase in temperature as being a unique state acquired by every body when it receives an increment of energy in the form of increased activity of the highly disorganized motions of its ultimate particles. Increments of energy of other forms, mass velocity, magnetization, electrification, chemical separation, etc., do not produce the same state or any of the striking phenomena characteristic of it.

In this connection I am forced to ask the question, if great elevation of temperature may not so increase the velocities of atoms and the electrons within the atoms, that the masses of these latter become increased, and so the total mass of the highly heated body? Is the mass of a solid cylinder of tungsten at  $3000^{\circ}$  C. the same as at  $0^{\circ}$  C.? With modern apparatus and methods the experiment is triable.

Profound modifications of the properties of matter, often so great as to make any given portion of matter unrecognizable as the same thing, are the invariable accompaniments of a great rise of temperature—that is, of a great increase in the disorganized motions of ultimate particles. With sufficient rise of temperature the permanence of any object is lost. High temperature, in short, makes of most kinds of matter something which is entirely new; something unrecognizable as the same stuff with which we started at ordinary temperature. What undreamed of beneficent uses may not matter possess in this new dress, put on with fire!

The very conception, on the other hand, of low temperature is a picture of quiescence. The particles of matter move in short, mean paths and sluggishly. Configurations established at higher temperature are not broken up. A change of atomic partners between molecules does not occur. If the temperature falls to that of liquid helium, the motions of the molecules and atoms practically cease. The properties of a mass are greatly modified, it is true, from what they are at ordinary temperature, but the particular fact to be noted is, that with diminution of disorganized motion few property changes occur which become permanent in



the sense that when ordinary temperature is restored familiar ordinary properties do not reappear.

I do not under-rate the high value of low temperature research on the properties of matter. By such research we have penetrated deeply into a further understanding of the constitution of matter. We have discovered by such research super-conductivity, and have discovered the means of extracting helium gas in quantity; but the upper limits of the temperature scale fascinate me more, for there matter pulsates with mighty energies. It takes on aspects and strange qualities that fascinate, and the hope is ever held out of discovering in the region of high temperature unsuspected properties of matter extremely useful in the everyday affairs of industry.

Our store of knowledge, embodied in tables of constants, physical and chemical of the properties of matter above  $1500^{\circ}\text{C}.$ , quantitatively expressed, is small indeed. Outside its property of giving off radiant energy, physicists and chemists have given little attention to a quantitative examination of the properties of matter exhibited at the higher temperatures. For a temperature exceeding  $1000^{\circ}\text{C}.$ , very little precise information is anywhere obtainable regarding such familiar properties as surface tension, molecular cohesion, molecular adhesion, thermal expansion, specific heat, latent heat of fusion, viscosity, compressibility, elasticity, and thermal conductivity. Thermal e.m.f.'s of combinations of high fusion metals and alloys, melting and boiling points of many elements and some compounds have been studied for the higher laboratory temperatures. The resistivities of most of the non-ferrous metals have been observed by the speaker at temperatures where the metals become molten, and above—but the quantity of this data is surprisingly small. That this is so is the more surprising when we pause to consider the relative simplicity of the property manifestations of matter when at high temperature. “By passing to the high temperature range we at once eliminate from consideration all such phenomena as crystallization, magnetism, surface coloring, production of aqueous solutions, the greater part of the phenomena of organic chemistry, and a multitude of other familiar physical and chemical manifestations. The science of biology outside the range of ordinary temperatures is non-existent.



"When nature is studied, simplified, so to speak, we should be able to acquire a better understanding of the increasingly complex phenomena which appear as we bring the lower temperature range up and the higher temperature range down. In the light of our knowledge of nature simplified we shall be better able to interpret her more complex manifestations at ordinary temperatures."<sup>5</sup>

We cannot afford, though we consider commercial demands only, to let our tables of constants for the higher temperature ranges continue to be filled as now, with blanks in the columns.

III. Primary effects produced by great elevation of temperature in a furnace are to volatilize any readily volatilizable substances which may be present, to greatly enhance chemical activities and to promote chemical interchange of atoms. At a very high temperature the disorganized motions of ultimate material particles are so intense that a species of evaporation takes place from the surface of many highly refractory materials, loading the atmosphere of the furnace with imperfectly gasified matter. The particles of this gas may not even be molecules, but rather groups of molecules or very minute masses analogous to the carbon particles in smoke or a flame. This is notably the case where Acheson graphite is heated above  $1500^{\circ}$  C. If a glazed porcelain tube be held for a short time only in a chamber with graphite walls, thus heated, the glaze becomes blackened with the flying particles of carbon that strike and stick to it. A wire of pure tungsten held in such a chamber soon becomes brittle from carbon absorbed from the hot atmosphere. Lining the inside walls of the chamber with highly refractory non-carbonaceous material, as magnesia, will not entirely prevent these effects.

It is observed in tungsten filament lamps that the tungsten evaporates with long exposure to high temperature. Gold evaporates rapidly at a temperature considerably below its boiling point.

At extremely high temperature, almost any two compounds which differ chemically, thoria and magnesia, for example, will react when in contact.

It may be safely assumed that no refractory is pure in the sense that it will not yield vapors from slight impurities more volatile than the refractory itself, unless such refractory has been preheated to, and for some time held at, a temperature higher

---

<sup>5</sup> "A Classification of High Temperature Physical Problems," by E. F. Northrup, *Chem. and Metal. Eng.*, March, 1915.



than the temperature at which it is afterward used. Thus all materials which are to be employed as containers or heat insulators should be treated to a higher temperature than that at which they are to be used, if freedom from chemical contamination is to be secured.

If metals are to be melted and great freedom from chemical contamination is demanded, they should be fused preferably in a container made of their own oxide, where such melts higher than the metal. Thus chromium oxide would be ideal for holding molten chromium, nickel oxide for molten nickel, aluminum oxide for aluminum, etc. Where the oxide of the metal itself is not suitable, a stable oxide as magnesia or thoria should be selected, and this should be greatly preheated before using it as a container. Metals, for instance, of the platinum group may be melted in a crucible made thus without contamination.

As contamination of the product may come from gases in the furnace, melting in vacuum is often employed. It is here suggested that a substitute for vacuum melting would be to bathe the furnace chamber with pure helium gas—which forms no chemical unions.

Oxides cannot be highly heated or melted in a graphite container because most of them are reduced by the graphite, and those not reduced become blackened. A tungsten crucible heat-insulated with pure thoria is suggested as a suitable electrically conducting container for melting several refractory oxides.

By developing heat directly in the product to be heated or in the crucible wall that contains it, there is no necessity that any part of the furnace chamber shall be hotter than the product itself. As the tendency to chemical contamination increases rapidly as the temperature mounts, any arrangement whereby the charge is the hottest part of the furnace, is an important safeguard against it.

Moissan in his classic work pretty fully examined the field of high temperature chemistry and the phenomena exhibited by matter up to a temperature where lime fuses. But the value of his work was greatly diminished by one important limitation set by the nature of his furnace. This furnace was a carbon arc furnace. Carbon was always present in the atmosphere of his hot chamber, and carbides were almost invariably formed at the high temperatures at which he worked. The properties of chemically pure metals of the tungsten group were unknown to him.



In the new high temperature research of to-day, means will be employed for studying matter under controlled conditions that will avoid the clouding effects on all precision work that results from chemical contamination.

IV. The modern tools which may be used in high temperature research may be classified under: Apparatus which focuses radiation from the sun, hot flames, the electric arc, and the electric resistance furnace, vacuum bulbs which heat a surface by electron impact, and the high-frequency induction furnace.

Hot flames heat a body at its upper surface or they heat a chamber, and the heat must flow through the wall of a crucible or container to reach the product being treated. The produced temperature, therefore, must be higher than the used temperature, while the wall of the container must be sufficiently refractory to withstand the higher temperature at its outer surface. The products of combustion from a hot flame invariably subject the material being heated to contaminating influences.

I am not informed on the use which may have been made of focused sun's rays to heat a small chamber to a high temperature. The method appears as one which offers many advantages where circumstances and the hour permit of its use. Very high temperature could certainly be obtained in an oxidizing atmosphere.

The electric resistance furnace may be constructed to be free from many limitations and most objections. Where the resistor is made of a non-carbonaceous material, the temperatures ordinarily obtained are not high. However, a small chamber may be heated to a very high temperature without carbon being present, by using molybdenum or tungsten as a resistor. The tungsten tube furnace is well known. If better and less elaborate means were not available for obtaining very high, carbon-free temperatures, a furnace of this character would serve well for many kinds of investigation.

The carbon arc furnace, which is the classical device for high temperature study, is limited in usefulness because carbon is present, and the temperature, extraordinarily high, is generated in a space of very small volume. Purity of product and controllable, uniform heating are not possible. Arcs between electrodes of semi-conducting oxides and high fusing metals have been considered, but I know of no practical applications to research having been made of such.



A focused stream of electrons will give a very high temperature where it impinges, but the volume which can be heated is small, and the necessity of working with a vacuum bulb will effectually eliminate this method for obtaining practical results.

The last method, that of high-frequency induction, is in my opinion the final and the ideal method for the production under controllable conditions of any temperature from room temperature up to that of melting tungsten; especially when carbon free conditions and complete freedom from chemical contamination are required. The high temperatures obtainable, furthermore, are not localized, as in the case of an arc, to a small volume; for a space of dimensions, limited only by the electric power available, may be heated throughout its extent with uniform temperature, and the final temperature obtainable is limited not by the method, but by the refractory properties of the walls which enclose the heated zone.

It is interesting to briefly consider the fundamental principle of this method of raising the temperature of a body within an enclosure of electrically non-conducting walls. Thus, heat is said to pass from one body to another by conduction or radiation, or by both. A body also acquires heat by an internal conversion of the kinetic energy of an electric current into heat energy. Again, ferrous materials acquire heat energy by rapid reversals of their magnetism. These are more or less arbitrary classifications of the means by which a body acquires heat. If thoughtfully considered, I think it will be recognized that in all cases where a body receives heat in any other way than by direct contact with a body at higher temperature, it receives its heat primarily as an influx of electromagnetic energy. The body absorbs the electromagnetic energy which is converted within the substance of the body into that particular form of energy, which consists of highly disorganized motions of the particles and which we call heat energy. Thus radiation from the sun warms a body on which it falls, and this radiation is electromagnetic energy of short wave-length. Artificially produced electromagnetic radiation, the long wave-length radiation of radio transmission, when it falls on any body that can absorb it, heats it. The heating occurs, but as a rule, not so rapidly, when the electromagnetic waves are of great length.

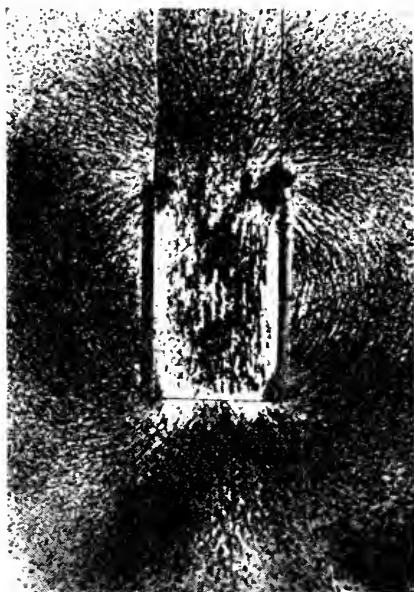
If a solenoidal coil is traversed by a current which varies rapidly in magnitude the space within and surrounding the sole-



noid is alternately stored with and depleted of electromagnetic energy. This electromagnetic energy is represented by the field of force in and around the coil. The field is made visible by iron filings. The field due to a cylindrical solenoid is here shown.

If a body is placed in the solenoid, electromagnetic energy falls upon it. If the current through the coil is rapidly alternating, electromagnetic energy impinges continuously upon the body. If the body nearly fills the interior of the coil, then a large part of the electromagnetic energy which flows into the interior of

FIG. 1.



Magnetic field associated with a current-carrying single layer solenoid ; made visible with iron filings.

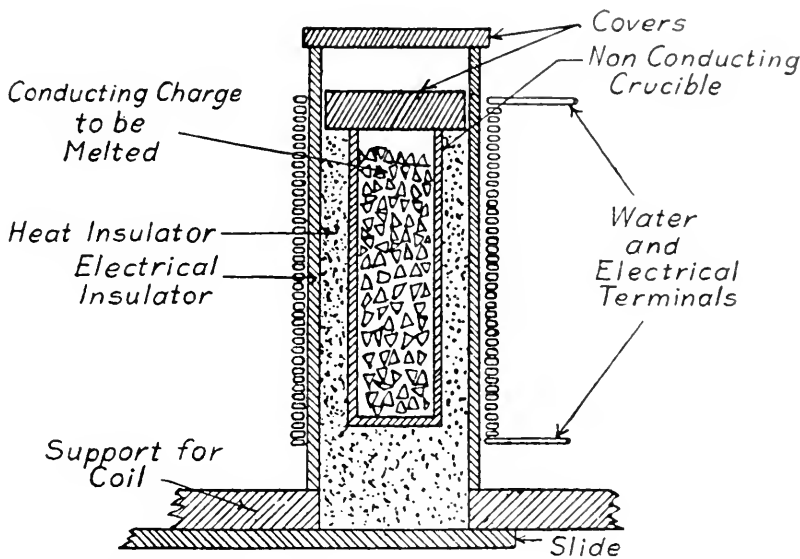
the solenoid falls upon the body. If the body were perfectly conducting, all the electromagnetic energy which falls upon it would be reflected from its surface. If the body were a perfect dielectric, none of the energy falling upon it would be absorbed. If the body is suitably conducting then all the energy which falls upon it penetrates toward its interior being absorbed, that is, converted into heat energy, as it penetrates deeper and deeper. If the conductivity of the body is favorable all of the electromagnetic energy which enters the body is completely changed over into heat energy—and the temperature of the body rises. With constant ampere turns in the coil the rate of absorption of electromagnetic energy will be proportional to the frequency of the current. The temperature of the body will rise rapidly if it receives



energy rapidly, and will go on mounting until the body loses energy in the form of short wave-length heat radiation, as rapidly as it receives energy in the form of long wave-length electromagnetic radiation. The body accumulates heat and experiences a rise in temperature because the heat insulators which surround it are perfectly transparent to long wave-length electromagnetic radiation, and nearly opaque to the short wave-length radiation emitted by a hot body.

In this method of heating—by influx of long wave-length electromagnetic energy—the body is not joined to a source of

FIG. 2.



High-frequency induction furnace loaded with small pieces of electrically conducting material contained in a chamber with walls of non-conducting, non-carbonaceous material. Local eddy currents are induced in the individual pieces of broken material, and through the mass as a whole. These currents rapidly heat the material, and, if of a fusible nature, the entire mass is soon melted. Pure iron or platinum is readily melted in this manner, and broken pieces of pure molybdenum have likewise been fused at an estimated temperature of  $2550^{\circ}\text{C}$ .

e.m.f. by electrical connections. It requires no electrodes. It can be enclosed hermetically in a vessel of dielectric material (quartz-glass, for example). This vessel can be filled with any non-metallic liquid, or any gas at any pressure which the vessel will endure, or it can be completely evacuated of everything except the body being heated.

Can any method be conceived of heating a body which is more ideal, if its actual realization in practice can be effected?

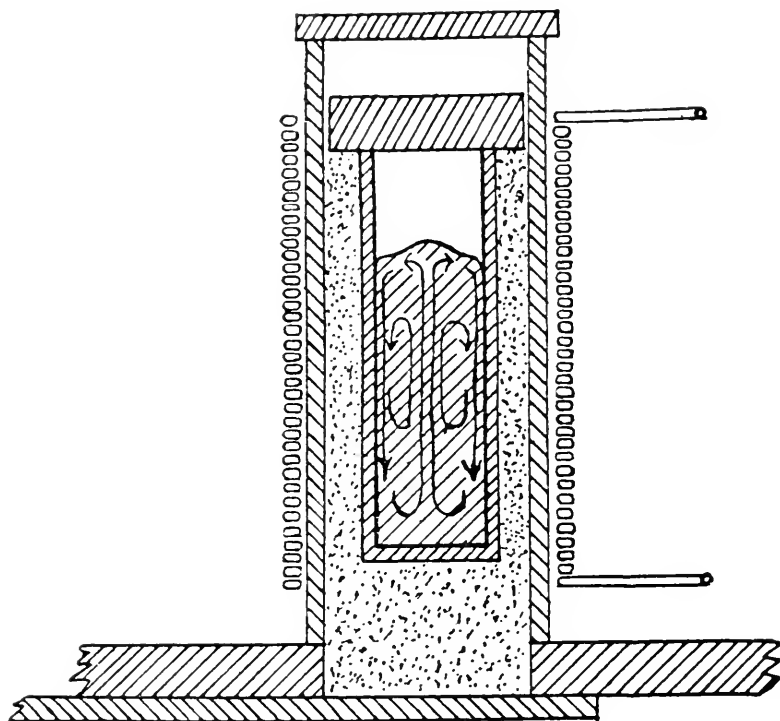
V. Six years of study with much experimentation and over three years of manufacturing activities have demonstrated that the method is realizable in practice and easily so.



The details of the methods employed have been frequently described and are well known, therefore, I can only give a word here to their elucidation.

The solenoidal coil, or inductor, is generally made of a one-layer winding of flattened copper tubing from  $\frac{3}{8}$ " to  $\frac{1}{2}$ " in diameter. It is wound edgewise to form a cylindrical or cone-shaped coil. The inside of the solenoid is lined with a thin layer of electrically insulating material as quartz-glass, Pyrex glass, micanite, or

FIG. 3.



Here is shown in cross-section the appearance of a metal or alloy after fusion is complete. The surface of the melt is elevated at its centre. The metal circulates, rising in the region of the axis and descending in circumferential region.

This stirring of the metal is not caused by heat, but by a mutual attraction of the current elements, the electric current induced in the melt being of greater density in the circumference of the melt than at the axis. The repulsive action of the primary upon the secondary also contributes to the stirring. This automatic circulation of the melt insures a perfect mix when alloys are melted.

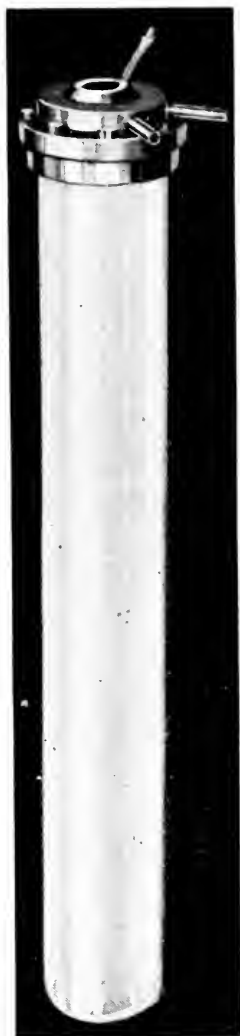
asbestos board. The body to be heated is preferably chosen cylindrical or somewhat tapered when used with a conical inductor. Its outside diameter is selected to be two-thirds to three-fourths the inside diameter of the solenoid. It is placed centrally in the solenoid, and the small space between the body and the sheathing of electrical insulation which lines the inside of the inductor is filled in with finely powdered, highly refractory material. This serves as a heat insulator. A water circulation is maintained



through the hollow, flattened copper tubing which constitutes the winding. This keeps the coil cool though molybdenum be held molten within the coil.

The frequency of the electric current passed through this

FIG. 4.



This shows a quartz tube closed at the bottom, and capped with a metal cover at the top. The metal cover is water cooled. The material to be heated is placed in the lower half of this vacuum chamber. The tube fits in the inductor coil shown in Fig. 2 and Fig. 3. The air is exhausted and melts are made in vacuum.

inductor is chosen high, 5000 to 50,000 cycles per second. Twenty thousand cycles is commonly employed.

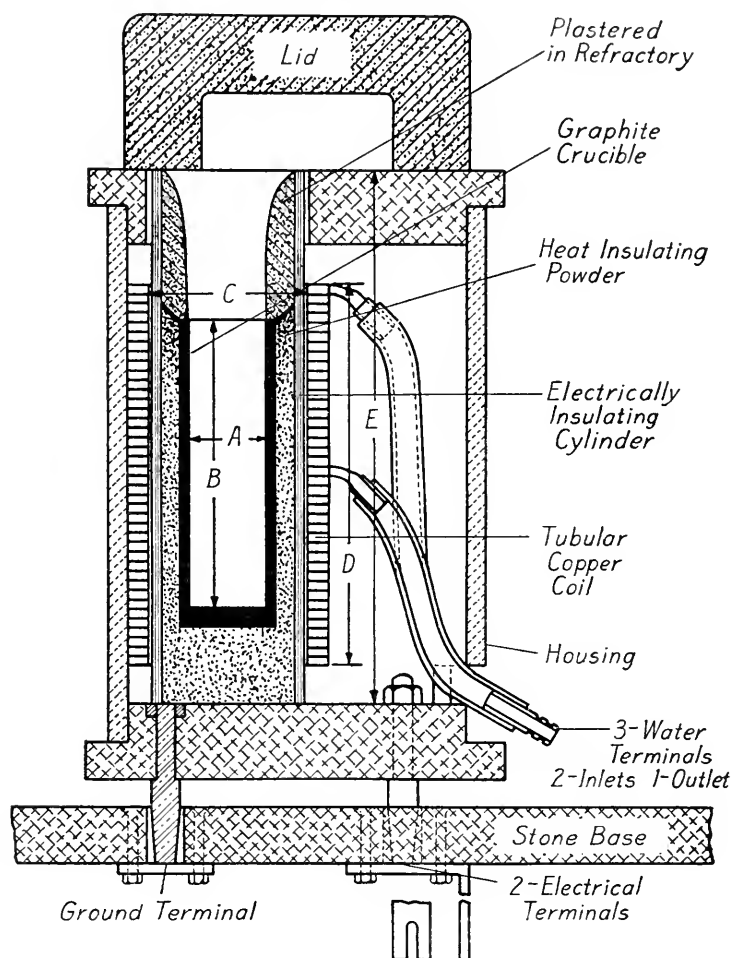
Over 1000 k.w. are to-day in service heating bodies in the above fashion. If the effectiveness of the method were better appreciated, many times this amount of high-frequency power



would be used for high temperature research and for the commercial heat treatment of materials.

In melting operations the method has almost no limits imposed. Thus in actual practice 50 ounces of chemically pure platinum have been melted from a cold start in six minutes and, most important to note, entirely free from any chemical contamination.

FIG. 5.



Convenient form of high-frequency induction furnace for general research and for melting precious metals—gold, platinum, etc. The dimensions of the chamber are: A, 5 cm. (2"); B, 19 cm. (7½"). The furnace may be lifted from its base and the contents poured.

Pure iron alloyed with a large percentage of tungsten, molybdenum, etc., is being readily melted, and always carbon free, and without other chemical contaminations.

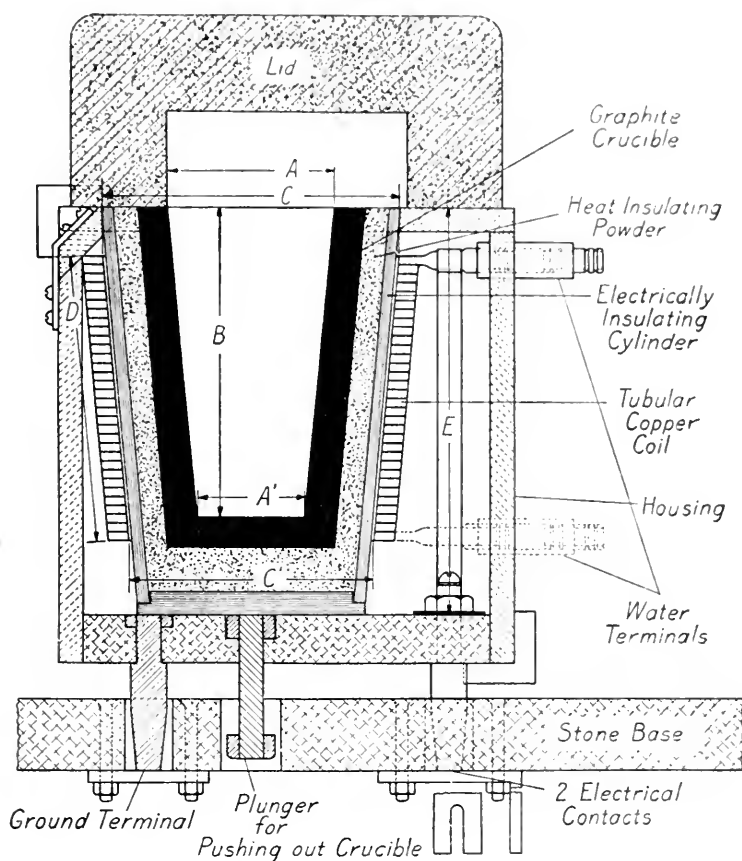
A very pure nickel-iron alloy, called permalloy, is being melted in crucibles holding 100 pounds by high-frequency induction at the rate of about 1200 pounds per day. Lower melting metals, silver, for example, are being melted in 600-pound charges.



Chambers with a wall of Acheson graphite one-fifth of a cubic foot in volume have been easily heated uniformly to a temperature which will graphitize carbon, and with an expenditure of only about 16 k.w.

Black-body chambers, which perfectly fill the conditions of the ideal black body for all manner of radiation experiments, are

FIG. 6.



Crucible type furnace used for melting or heating in a graphite chamber. Dimensions, A, 9 cm. (3.5"); A', 5.6 cm. (2.25"); B, 16 cm. (6.5").

This furnace is particularly suited to melting silver, gold, copper and their alloys. The furnace may be lifted from its base and the contents poured.

readily heated to a temperature little short of the carbon arc. If the chamber walls are of tungsten, carbon need not be present.

Some form of generator of high-frequency current to supply high-frequency power to the furnace is required, or some form of frequency converter must be used which will receive power at a commercial frequency, and deliver it at a high frequency. Apparatus of both above types are now available. For research work in the laboratory 15 kv-a. and 35 kv-a. converter sets are standardized manufactured articles. Large power sets delivering



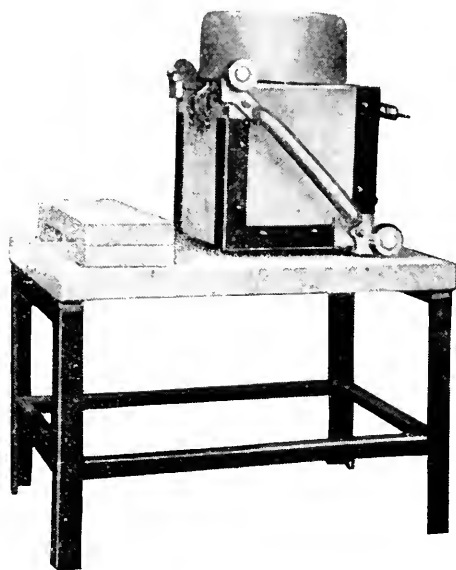
several hundred kilowatts of high-frequency power may be obtained when the commercial requirements justify the rather high cost of such equipment.

VI. No sharp lines separate low, ordinary, medium, and high temperatures. I shall call research work on the properties of matter when over  $1000^{\circ}$  C. high-temperature research.

The outstanding problems are naturally grouped into:

1. *High-temperature Chemistry*.—Here we have to consider the relative affinities of the elements when at high temperature;

FIG. 7.



Assembly view of furnace shown in Fig. 6. The side handles are grasped by the hands. The furnace is lifted from its base and the contents poured. This and the other furnaces shown are not above room temperature on the outside.

what new combinations of elements will form at different high temperatures, and which of such new-formed combinations remain unaltered when the temperature is brought back to ordinary.

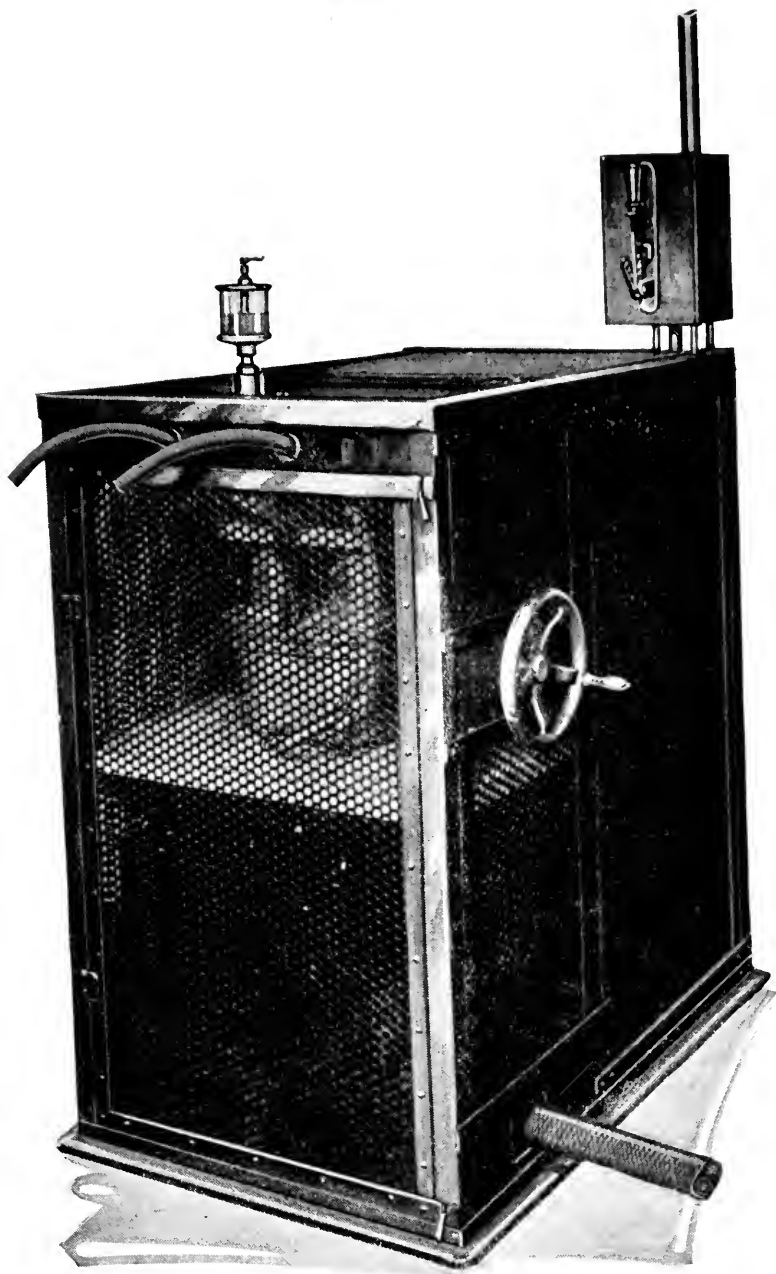
High-temperature chemistry, though a very simple chemistry, has heretofore presented great difficulties in the matter of maintaining the elements and compounds under study pure. Thus accurate quantitative determinations as yet are very few. The inductive method of heating will help greatly to remove these difficulties.

2. *The Physical Properties of Matter*.—(a) While under the condition of high temperature; and (b) the new physical proper-



ties which remain at ordinary temperature, which the high-temperature treatment imparts.

FIG. 8.



General view of a 15 kv-a. high-frequency converter. This converter is placed between the current source and the furnace. It is used to change current of commercial frequency (received at the switch box shown at the top) into current of high frequency. This current is delivered by the terminals shown at the base on the right. It has no moving parts. It will supply high-frequency power for operating any of the furnaces shown in Figs. 2, 3, 5, 6, and 7.

As physical properties are very sensitive to chemical impurity, and as chemical purity at high temperature has been seldom



obtained in the past, there is great need of trustworthy information along this line.<sup>6</sup>

3. *Phenomena of Electronic Emission from Bodies at High Temperature.*—This is an extensive field for exploration into the region of high temperature. Thus far investigation has been chiefly confined to a study of electronic emission from hot tungsten filaments in vacuum. It is probable that all matter freely emits electrons when above  $1500^{\circ}$  or  $1600^{\circ}$  C., and that no electrical insulation is possible at and above these temperatures. The free emission of electrons from the surface of the sun, giving rise to many terrestrial and astronomical phenomena of interest, is one phase of the subject.

4. *Radiant Properties of Matter at Very High Temperature.*—This is one field of high-temperature research that physicists have much investigated. The means which are now offered for producing, with or without carbon present, a truly black-body temperature of great elevation and throughout a considerable volume in a vacuum or in any atmosphere at widely selected pressure ought to furnish great aids in a further pursuit of this line of inquiry.

VII. In conclusion, I wish to state that I have made an earnest effort to make an inventory in my mind of every avenue of physical and chemical research which promises to lead rapidly to new information of high value. I give it as my belief, after many years spent in the laboratory, that no path goes straighter or quicker to discoveries which will add much to our knowledge of matter itself, and to the finding of things useful for everyday life, than the roadway of high-temperature investigation.

I make an appeal to this generation of young, enthusiastic investigators who are students of physics and chemistry, to turn their attention and direct their efforts to a study of the region of the higher temperatures. This branch of physics and chemistry is very properly named electrothermics. Tools for work in this region are developed, and great advances in science will surely follow when departments of instruction lecture on this subject, and laboratories become equipped for experimental investigations in this fascinating and fruitful territory.

---

<sup>6</sup> Reference is suggested to "A Classification of High Temperature Physical Problems," by Edwin F. Northrup, *Chem. and Metall. Eng.*, March, 1915.



# SOLUBILITY OF MANNITE IN MIXTURES OF ETHYL ALCOHOL AND WATER.\*

BY

HENRY JERMAIN MAUDE CREIGHTON,

Member of the Institute,

AND

DAVID S. KLAUDER, JR.,

Department of Chemistry, Swarthmore College.

IN the course of another investigation, it was necessary to know the solubility of mannite in mixtures of ethyl alcohol and water at several different temperatures. Since the data available were very meagre,<sup>1</sup> determinations have been made in this laboratory of the solubility of mannite in aqueous alcohols varying from 0 to 100 per cent. ethyl alcohol, at a number of temperatures between 0° and 60°.

The mannite ("Kahlbaum") used in these experiments melted at 165.9°. The alcohol employed for the solubility determinations in this solvent alone was prepared by drying 99 per cent. ethyl alcohol over lime for several months and then fractionating. The boiling point, density and refractive index of this alcohol were determined as criteria of its purity and had the following values:

boiling point = 78.27° (760 mm.)

$d = 0.78509$

$n = 1.35954$

The different mixtures of alcohol and water were prepared by diluting 93 per cent. alcohol with the requisite amount of water.

The weight of mannite contained in a known weight of saturated solution was obtained by evaporating the solution to dryness in platinum dishes on a water-bath, drying at 110–120° and weighing the residue. Saturation in pure water and in pure ethyl alcohol was attained by boiling the finely powdered mannite and

---

\* Communicated by Professor Creighton.

<sup>1</sup> Berthelot, M., *Ann. Chim. Phys.* [3], 47, 301 (1856); Krusemann, H. D., *Ber.*, 9, 1476 (1876).



FIG. 1.

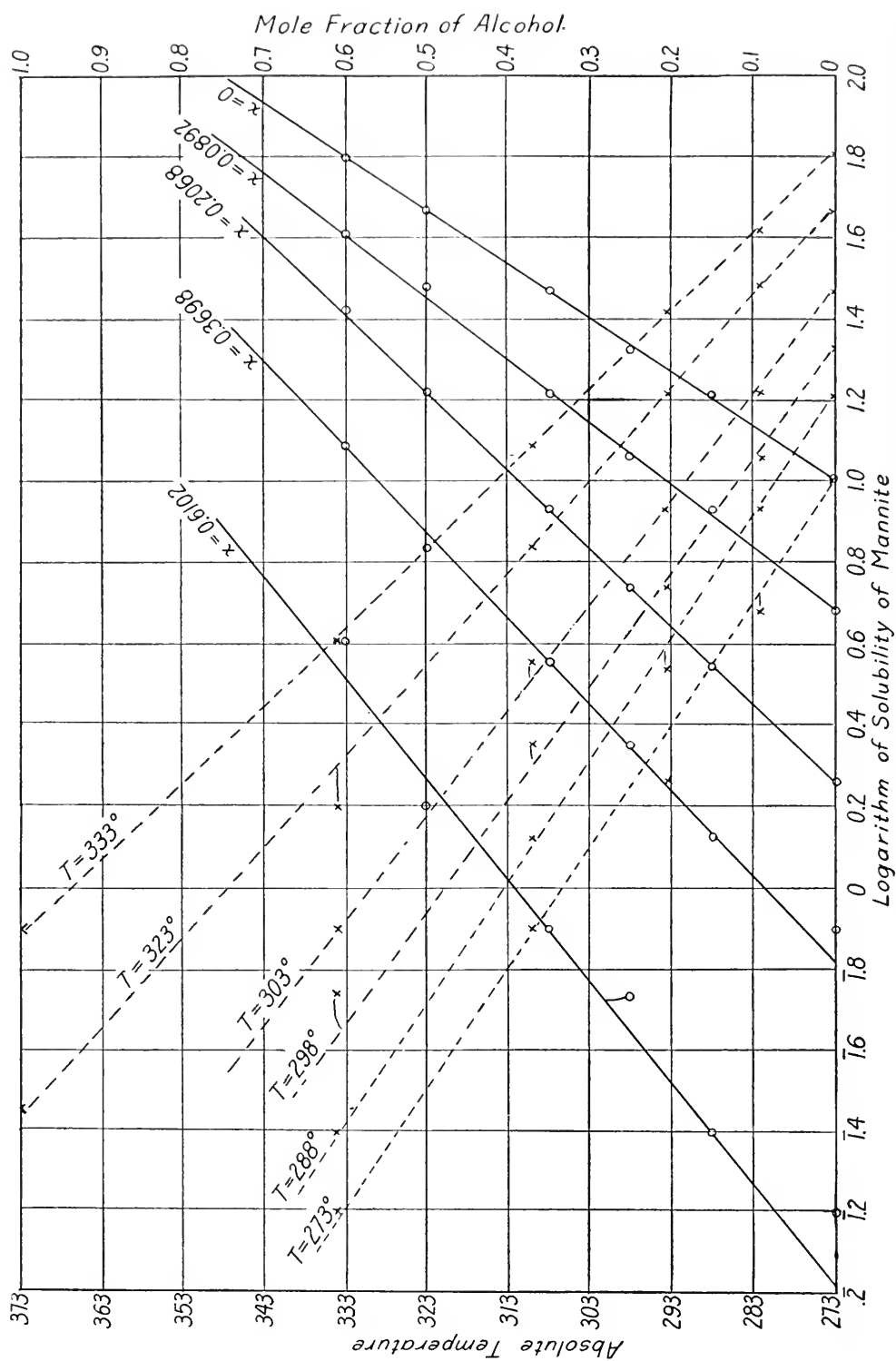




TABLE I.  
*Solubility of Mannite in Mixtures of Alcohol and Water.*

Per cent. by Weight of Alcohol.	0	20	40	60	80	100
Mole Fraction of Alcohol.	0	0.0892	0.2068	0.3698	0.6102	100

Tempera- ture, °C.	Solubility in Grams per 100 Grams of Solvent.									
	Ob- served.	Calculated.		Ob- served.	Calculated.		Ob- served.	Calculated.		Calcu- lated.
		a	b		a	b		a	b	a
0	10.2	5.00	4.01	1.81	1.05	1.00	0.79	0.53	0.50	0.003
15	16.4	8.71	8.27	3.49	3.78	3.58	1.33	1.19	1.06	0.014
25	21.3	11.03	11.81	5.48	5.50	5.48	2.25	1.02	1.88	0.031
35	29.6	17.19	17.35	8.60	8.71	8.50	3.62	3.35	3.21	0.081
50	47.2	30.20	29.00	16.76	16.70	16.36	6.92	7.43	7.00	0.32
60	61.14	43.29	41.86	26.50	25.8	26.1	12.36	12.59	12.73	0.78



solvent for several hours in a flask having a reflux condenser. The mixture was then transferred to a bottle fitted with a stirrer which turned in a mercury seal (thus preventing loss of solvent by evaporation or admission of moisture from the air), and cooling to the desired temperature in a thermostat. Subsequently, the mixture was stirred at this temperature for five hours. In the aqueous alcohols, saturation was effected by stirring the mannite and solvent for some time at 5 to 10° above the temperature at which the solubility was to be determined. The mixture was then cooled to, and kept at, the desired temperature for a period of six to seven hours, stirring being continuous. At the end of the times mentioned, a portion of the solution was removed for analysis. Stirring was continued for two hours longer, when a second portion of the solution was removed. The weights of mannite contained in equal weights of these two portions agreed closely. The results of the solubility measurements, which represent the mean of these two weights, are contained in Table I and represented graphically in Fig. 1, where the logarithm of the solubility is plotted (1) against the absolute temperatures for different concentrations of alcohol (solid curves), and (2) against the mole fraction of alcohol for the different temperatures (broken curves). Both sets of curves are approximately linear.

The logarithm of the solubility of mannite ( $\log S$ ) in alcohol-water mixtures, at any temperature between 0° and 60°, can be expressed as a function of the solubility in pure water ( $a$ ), the mole fraction ( $x$ ) of alcohol in the solvent and the absolute temperature ( $T$ ), *i.e.*,

$$\log S = \log a + dx + gtx, \quad (a)$$

where  $d = -10.57$  and  $g = 0.0260$ . At a particular temperature between the above-mentioned limits, the logarithm of the solubility of mannite in mixtures of alcohol and water can be expressed as a function of the solubilities in the pure components and the mole fractions of the components, *i.e.*,

$$\log S = (1-x)\log a + x\log b, \quad (b)$$

where  $a$  and  $b$  represent the solubility of mannite in pure water and pure ethyl alcohol, respectively. Solubility values calculated by means of equations (a) and (b) are recorded in Table I in the



columns marked "a" and "b." It will be observed that, with a few exceptions, the calculated values agree fairly well with those determined by experiment.

#### SUMMARY.

1. The solubility of mannite in alcohol-water mixtures, containing 0, 20, 40, 60, 80 and 100 per cent. of ethyl alcohol, has been determined at 0, 15, 25, 35, 50 and 60°.

2. Within the temperature range studied, the logarithm of the solubility of mannite in mixtures of ethyl alcohol and water at any temperature is a function of the solubility in pure water, the mole fraction of alcohol present in the solvent and the absolute temperature; while at a particular temperature, it is a function of the solubilities in the pure components and the mole fractions of these components.

Swarthmore, Pennsylvania,  
March 1, 1923.

---

**Measurements of the Aurora of March 22-23, 1920.** CARL STOERMER. (*Comptes Rendus*, January 8, 1923.)—On March 22-23, 1920, there occurred an aurora of the first order in respect to extent and splendor. It was accompanied by violent magnetic perturbations and by the passage of a large group of sun spots, and was characterized by the length of its rays and the variety of its colors.

Several rays situated above the Shetland Islands and Trondhjem were photographed from stations a long distance apart. The length of the base assures the accuracy of the results deduced. The upper ends of the rays were computed to lie from 550 to the enormous height of 750 km. above the earth. Later in the night other rays were photographed. Their lower ends were calculated to be elevated above the earth by distances never less than 100 km. and ranging from 100 to more than 300 km. Along those rays of which the lower ends were more than 120 km. above the earth there was not much change in brightness, but along those rays having their lower ends at a height from 100 to 120 km. above the earth the lower part was much brighter than the upper portions. "This is well explained by the hypothesis that the composition of the air changes rapidly in this interval from an atmosphere of nitrogen below to one of helium and hydrogen above." The lower border of one auroral drapery was not more than 85 km. above the earth. It reached 16 km. upwards.

The elevations here given are in striking contrast to data published in early volumes of *Nature* according to which two companions in high latitudes had streamers of the aurora flickering between them as they walked.

G. F. S.



**Cells with Fluorescent Liquid.** A. GRUMBACH. (*Comptes Rendus*, January 8, 1923.)—Two platinum electrodes in a fluorescent solution constitute an electric cell when one of them is illuminated. In 1908 Goldman experimented on such cells, using saturated solutions of the fluorescent solute. He noted an electromotive force only upon illumination of the electrode. The present experimenter, however, using dilute solutions gets the effect in a different way. The cell was kept in the dark. A portion of the solution was exposed for two hours to the light from a mercury arc which had been filtered through a layer of water. Then one c.c. of this liquid was introduced into the cell near one of the electrodes. Immediately an electromotive force manifested itself and in its decay with time followed the curves got when an electrode was directly illuminated with subsequent removal of the light. The author interprets this as proving that the seat of the effect is not at the surface of the electrode.

When a solution of uranine was used, .05 g. per 100 g. water, the illumination of an electrode at first made it negative. The electromotive force grew larger and larger with the passage of time until after  $21\frac{1}{2}$  minutes it amounted to 8.2 millivolts. At the end of 40 minutes, the illumination continuing, the same electrode had become positive with an e.m.f. of 11 millivolts. This rose with increasing slowness until after 133 minutes it amounted to 100 millivolts. Then the cell was put in the dark, where the e.m.f. continued to rise for several minutes. It later diminished. G. F. S.

**The Absence of Oxygen and Water-vapor from the Spectrum of Venus.** C. E. ST. JOHN and S. B. NICHOLSON. (*Astrophys. J.*, December, 1922.)—It has been commonly assumed that Venus has an atmosphere resembling that of our earth in the possession of both oxygen and water, but recently the correctness of this belief has been questioned.

When the spectrum of Venus is photographed there are found dark lines due to oxygen. It is known that there is oxygen in the atmosphere of the earth and this would by itself produce such oxygen lines. The problem is to make the oxygen of Venus, if it really exists, write its autograph on the plate in an unimpeachable manner. The Mount Wilson astronomers accomplished this by taking their photographs at a time when the earth and Venus have such a relative velocity that the shift of the Venus lines corresponding to the Doppler effect amounted to  $.268 \text{ \AA}$  toward the violet, "an amount sufficient to separate completely the terrestrial components from those of Venus." The same reasoning applies to the search for water lines. "No trace of any line due to the planet's atmosphere was observed. It is estimated that in the path traversed by the solar light through Venus' atmosphere there must be less than the equivalent of one metre of oxygen, less than one-thousandth of that in our atmosphere, and less than one millimetre of perceptible water-vapor." G. F. S.



## NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

### UNITED STATES GOVERNMENT SPECIFICATION FOR DRY CELLS.<sup>1</sup>

THIS circular contains specifications for dry cells, flashlight batteries, and radio B batteries. The dimensions of the standard sizes are given, followed by a discussion of standard tests and the minimum required performance for each of the standard sizes. Dry cells in excess of 100,000,000 are used annually in this country, and, although certain sizes have predominated, a large number of relatively unimportant sizes have been made. In an effort to standardize the more important sizes the Bureau of Standards called a conference of the leading manufacturers and largest individual users of dry batteries to meet with representatives of the various government departments in December, 1921. The conference considered seventeen different sizes of dry cells, and standardized seven of these sizes. It considered thirty different sizes of flashlight batteries and adopted eight of these as standard. It considered assembled batteries of the larger cells for ignition and similar work of which there are approximately thirty different sizes being made at the present time, and adopted six of these as standard. Two sizes of batteries for use with radio apparatus were also standardized. It is expected that the elimination of many sizes for which there is little demand, and which will no longer be considered standard, should result in considerable saving in the cost of manufacture and increase the convenience to the public.

A description of the manufacture and electrical characteristics of dry cells has been published in the second edition of Circular 79 of the Bureau of Standards.

---

### SOAP.<sup>2</sup>

[ABSTRACT.]

THIS circular contains a brief discussion of the general composition of soap and of the most important varieties of soap commonly used, together with an outline of certain manufacturing

---

\* Communicated by the Director.

<sup>1</sup> Circular No. 139, price five cents.

<sup>2</sup> Circular No. 62, price five cents.



procedures. Detailed specifications, including methods of sampling and testing, are given for special grade laundry soap, hard water laundry soap, and milled toilet soap.

**PROPOSED SPECIFICATION FOR SPECIAL GRADE LAUNDRY SOAP.**

This specification was prepared by the soap committee of the soap section of the American Specialty Manufacturers' Association in coöperation with a technical committee of the Federal Specifications Board, and is considered satisfactory for the grade of soap indicated. This specification has not been recommended for adoption as a government standard as there appears to be no demand at this time for soap of this kind in the government service. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by the Soap and Soap Products Committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a high-grade, well-made, uniformly mixed laundry soap, made from soda and fats; free from or with only a relatively small proportion of rosin; low in matter insoluble in alcohol; free from objectionable odor; and suitable for use with soft water for general cleaning and laundry purposes. Bidder shall state size, weight and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 34 per cent. Deliveries which yield more than 34 per cent. of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 5 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.2 per cent.

Matter insoluble in water shall not exceed 1 per cent.

Rosin shall not exceed 20 per cent.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constit-



uents will be calculated on the basis of material containing 30 per cent. of matter volatile at  $105^{\circ}$  C.

The material will be purchased by net weight, provided the matter volatile at  $105^{\circ}$  C. does not exceed 30 per cent. With deliveries containing more than 30 per cent. but not exceeding 34 per cent. of matter volatile at  $105^{\circ}$  C., settlement will be made on the basis of 30 per cent. of matter volatile at  $105^{\circ}$  C., *i.e.*, seven-tenths of a pound of non-volatile matter shall be considered one pound of soap.

**PROPOSED SPECIFICATION FOR HARD WATER GRADE LAUNDRY SOAP.**

This specification was prepared by the soap committee of the soap section of the American Specialty Manufacturers' Association in coöperation with a technical committee of the Federal Specifications Board, and is considered satisfactory for the grade of soap indicated. This specification has not been recommended for adoption as a government standard as there appears to be no demand at this time for soap of this kind in the government service. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by the Soap and Soap Products Committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a well-made, uniformly mixed laundry soap, made from soda and fats of which not less than 20 per cent. shall be coconut oil; free from rosin; free from objectionable odor, and suitable for use with hard water for general cleaning and laundry purposes. Bidder shall state size, weight, and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Color to match that of sample submitted for color only.

Matter volatile at  $105^{\circ}$  C. shall not exceed 44 per cent. Deliveries which yield more than 44 per cent. of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall be not less than 8 per cent. nor more than 20 per cent.



Free alkali, calculated as sodium hydroxide ( $\text{NaOH}$ ), shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 1 per cent.

The acid number of the mixed fatty acids prepared from the soap shall not be less than 205.

The percentage of matter volatile at  $105^{\circ}\text{C}$ . will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 38 per cent. of matter volatile at  $105^{\circ}\text{C}$ .

The material will be purchased by net weight, provided the matter volatile at  $105^{\circ}\text{C}$ . does not exceed 40 per cent. With deliveries containing more than 40 per cent. but not exceeding 44 per cent. of matter volatile at  $105^{\circ}\text{C}$ ., settlement will be made on the basis of 40 per cent. of matter volatile at  $105^{\circ}\text{C}$ ., *i.e.*, six-tenths of a pound of non-volatile matter shall be considered one pound of soap.

#### PROPOSED SPECIFICATION FOR MILLED TOILET SOAP.

This specification was prepared by the soap committee of the soap section of the American Specialty Manufacturers' Association in coöperation with a technical committee of the Federal Specifications Board, and is considered satisfactory for the grade of soap indicated. This specification has not been recommended for adoption as a government standard as there appears to be no demand at this time for soap of this kind in the government service. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by the Soap and Soap Products Committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a high-grade milled cake soap, as free as possible from water; either colored or uncolored and unscented or perfumed in a manner indicated in the contract; thoroughly saponified; well compressed in firm, smooth cakes of a size and shape specified in the contract. It should lather freely when used with cold water. Bidder shall state weight and number of cakes in each box.



Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at  $105^{\circ}$  C. shall not exceed 15 per cent. Deliveries which yield more than 15 per cent. of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 1.5 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1 per cent.

Matter insoluble in water shall not exceed 0.1 per cent.

Unsaponified saponifiable matter shall not exceed 0.1 per cent.

Rosin, sugar, and foreign matter shall not be present.

The color, odor, and character of soap must be as specified by the purchaser.

The percentage of matter volatile at  $105^{\circ}$  C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 15 per cent. of matter volatile at  $105^{\circ}$  C.

The material will be purchased by net weight.

---

#### ELECTRICAL CHARACTERISTICS AND TESTING OF DRY CELLS.<sup>3</sup>

THIS circular is a revision of the circular bearing the same title, which was issued by the Bureau of Standards, April 25, 1919. It includes decisions of the conference of leading battery manufacturers, representatives of government departments, and a few of the largest individual users of dry cells and flashlight batteries, which met at the Bureau of Standards on December 5, 1921. The object of this conference was to consider the standardization of sizes of dry cells and the revision of specifications for them. The circular also includes much additional data on the performance of dry cells which has been obtained since the first edition of the circular was issued.

The theory and construction of dry cells are discussed. Zinc in contact with a solution of ammonium chloride becomes negatively charged because of the departure of positive zinc ions from its surface. As the zinc dissolves during the discharge of the cell, zinc ions, ammonia, and hydrogen ions are produced. A mixture of ground carbon and manganese dioxide serves as the cathode

---

<sup>3</sup> Circular No. 79, second edition, price fifteen cents.



and depolarizer for the cell. This becomes positively charged, for which several explanations are offered. The zinc serves as the container for the cell and as an anode. The electrolyte consists of a water solution of ammonium chloride and zinc chloride, and it is held partly in an absorbent material that lines the zinc container and partly in the mixture of carbon and manganese dioxide. The electrolyte is therefore unspillable, which fact has given rise to the common designation "dry cell."

There are several different methods of construction. The most familiar method used in making the larger sizes of dry cells in this country is the so-called paper-lined method. Before the cell is filled with the depolarizing mixture a lining of pulp board is placed inside the can. After this the depolarizing mixture is tamped into the cell around the carbon rod, and the protruding part of the pulp board lining is folded down over the top of the mixture. After this the cell is sealed. Another familiar method of construction is found in the so-called "bag type" cells which are commonly made in Europe and are typical of the small flashlight type of cells made in this country. A carbon rod with a surrounding mixture of carbon and manganese dioxide is wrapped in muslin and tied with a string, forming a unit which can be placed in the zinc can leaving sufficient space between the two for the electrolyte in the form of a paste. Other methods of construction which are less commonly used are also described in the circular.

The large size of dry cells, of which the most familiar example is the cell  $2\frac{1}{2}$  inches in diameter by 6 inches in height, may be subdivided according to the class of service for which it is intended. There are the ignition or heavy service cells, the telephone or light service cells, and an intermediate class, which is commonly designated "general purpose cells." Fundamentally, these are all of the same general type of construction, but they embody features which make them peculiarly suited to the class of service for which they are designed. The so-called ignition cells are intended for use in ignition of internal combustion engines and other service requiring considerable current. The telephone cells are intended for light intermittent service, including bell ringing and similar work. Assembled batteries consist of two or more cells combined to form a unit for which certain voltages and types of battery are now recognized as standard. Flashlight batteries



contain cells which are commonly of the bag-type construction. There are three different types of flashlight batteries that are considered standard. These contain standard sizes of flashlight cells of which there are five. Besides these there are desiccated, partially assembled cells and several other forms that are found on the market.

The circular discusses the electrical characteristics of dry cells beginning with a description of the behavior of dry cells in a circuit and the influence which the internal resistance of the dry cells has upon its performance. Curves are shown for the increase in internal resistance during discharge. When dry cells are used in groups, it is desirable to arrange the group in such a way as to secure the most economical service. Two factors are involved. The first is the voltage requirement and the other the current requirement. When an arrangement of cells involving series and parallel connection is required, a choice arises in the method of connecting them, a series of parallel connected cells generally being preferred.

The effect of temperature on the open-circuit voltage of dry cells is small and for most purposes can be neglected entirely. The effect of temperature on the maximum current which the cell can deliver is an increase of approximately 1 ampere for each  $3^{\circ}$  C. rise in temperature. Heat produces deterioration of dry cells in two ways. It tends to produce leakage, and it increases the rate of chemical reaction including local action taking place within the cell. It is therefore desirable to keep the cells when in storage in a cold place. The effect of temperature on the service capacity of the cells is marked, and tables are given in the circular showing the variation in the duration of service which may be obtained under varying conditions of discharge.

Since dry cells are generally used in circuits on which the resistance is constant or nearly so, the capacity is usually expressed as the number of hours or days that the cell will continue to give service on such a circuit. The capacity of dry cells may also be expressed in terms of ampere-hours or watt-hours. The circular includes extended tables showing the capacity for standard makes of the No. 6 size of dry cells discharging through fixed resistances and at constant current rates to various cut-off voltages. It is found that for any cut-off voltage the efficiency rises to a maxi-



num as the resistance of the discharge circuit increases to about 100 ohms, but after this the efficiency falls off abruptly.

The standard tests for dry cells are described, and in an appendix specifications are given for dry cells, including all of the common types. These specifications emphasize the conditions which the cells must meet under test, but do not include manufacturing details.

---

#### A STUDY OF COMMERCIAL DIAL MICROMETERS FOR MEASURING THE THICKNESS OF PAPER.<sup>4</sup>

By Paul L. Houston and D. R. Miller.

[ABSTRACT.]

CONTROVERSIES frequently arise between the paper manufacturer or jobber and the consumer with regard to the thickness of paper. The cause of such controversies is usually traced to a difference in the readings of the instruments used in determining the thickness. Several types of dial micrometers are used in measuring paper. A study was made of the mechanism of a number of common types of dial micrometers to determine the effect of design on the performance and accuracy. Measurements were made of the static contact pressure and area and parallelism of the contacts. To determine the friction a measurement was made of the force required to move the mechanisms from rest towards increased readings of the pointer and the force that would just prevent movement towards decreased readings. One-half the difference between the force required to move the mechanisms to higher readings and prevent movements towards lower readings is evidently the friction of the mechanisms.

The total average contact pressure varies at a reading of 0.10 inch on different instruments from approximately 1½ ounces to over 11 pounds. Although the area of the plunger foot or contact is comparatively large for the higher total contact pressure, still the pressure per square inch varies from 2 to 43 pounds per square inch at the 0.10 inch reading. The friction of the mechanisms varied from a fraction of an ounce for an instrument with light moving parts and low contact pressure to over 3 pounds for an instrument with heavier parts and high pressure. In no instance was the plunger foot or contact parallel to the anvil over the

---

<sup>4</sup> Technologic Papers, No. 226, price ten cents.



whole surface to 0.0001 inch, that is, to one-tenth of the smallest graduation on the dial.

In two of the instruments, the required multiplication is obtained by two moving parts. In one of these the plunger carries a pin which engages with and causes rotation of a worm, to the end of which the pointer is rigidly fastened. The other instrument has a nut integral with the plunger, and a rotating screw engaged with the nut carries the pointer. The mechanisms vary from two moving parts to four moving parts. In the most common types of dial micrometers, the plunger is provided with a rack which engages with a train of gears or gear sectors. The pointer is fastened to the staff of the last gear in the train. The mechanisms of the instruments are illustrated diagrammatically and the number, length, and diameter of the bearings and the number and direction of action of the springs in each instrument is shown.

To determine if the variations in contact areas and contact pressures found had any bearing on the variation in values of thickness of paper obtained with various instruments, a performance test was made on nine micrometers. In this test fourteen different papers were used. To eliminate variation in the samples, thirty readings of the thickness of each paper were made with each micrometer. The readings of the instruments were corrected for errors found by comparison with standard steel thickness gages. Tables are given showing the average thickness of each paper as obtained with each micrometer and the deviation of the thickness of each paper obtained on each micrometer from the mean thickness as obtained by all the micrometers.

To show how the various papers are affected by the variation in contact areas and pressure represented by these nine micrometers, the total variation or difference between the highest average and lowest average value is shown for each paper. This total variation varies from 0.0003 inch for a high machine-finish writing paper 0.0025 inch thick, to 0.0010 inch for a sized and supercalendered ledger paper, 0.0065 inch thick. The machine-finish printing papers also show a high total variation when measured with this set of instruments. One of the instruments gave average values for the papers equal to or greater than the average obtained with all instruments. Two instruments gave average values equal



to, or less than, the average obtained with all instruments. The other micrometers show variations both plus and minus.

To further investigate the effect of contact areas and pressure on the measured thickness of the papers, a test was made of the compressibility of the papers with different sized contacts and various contact pressures with an instrument especially designed for the purpose. Curves are given showing the micrometer readings on each of the fourteen papers for three different contacts and total contact pressures, varying from 7 to 79 ounces. The reading of thickness showed variations of 0.0010 inch to 0.0015 inch between the low pressure (7 ounces) and the largest contact (0.314 square inch) and the highest pressure (79 ounces) and the smallest contact (0.0785 square inch).

A study of the results on the performance test and compression test shows that the same readings cannot be obtained with different contacts even if the same pressure per square inch is used. It is necessary then, to use both a standard contact and a standard contact pressure to obtain consistent results. To avoid difficulties in obtaining and retaining parallel contacts, it is suggested that the upper contact be made slightly convex.

The effect of design of the mechanisms on the friction, contact pressure, accuracy, and performance of the instruments is discussed, and specifications are laid down for a standard instrument. These specifications do not limit the standard instrument to any particular design, and it is felt that several of the types of mechanisms studied can be employed in instruments that will meet the specifications. This paper also contains specifications for procedure in determining the mean thickness of a sample of paper.

---

#### WAVE-LENGTH MEASUREMENTS IN THE ARC SPECTRA OF GADOLINIUM AND DYSPROSIUM.<sup>5</sup>

By C. C. Kiess.

[ABSTRACT.]

IN this article are presented wave-length data derived from a measurement of the arc spectra of Gd and Dy from about 5500 Å. in the green out into the infra-red. Spectrograms of very pure gadolinium oxide and dysprosium oxalate, prepared at the Univer-

---

<sup>5</sup> Scientific Paper, No. 466, price five cents.



sity of Illinois, were made with the large concave grating spectrograph of the Bureau of Standards. In addition to these plates, there were available for measurement, several spectrograms made by Prof. J. M. Eder of the gadolinium and dysprosium salts separated by C. Auer von Welsbach. The wave-length data not only confirm the results of the chemists in separating the compounds in a very pure state from the original materials, but give, also, an accurate description of the spectra in regions that have hitherto been only incompletely investigated. The two tables of wave-lengths contain, respectively, about 950 lines observed in the arc spectrum of gadolinium, and about 800 lines for dysprosium. This work completes the investigation of the original assignment of material from the University of Illinois. Two previous papers give similar data for yttrium, lanthanum, and cerium, and for neodymium and samarium.

---

**FURTHER TESTS OF STELLAR RADIOMETERS AND SOME MEASUREMENTS OF PLANETARY RADIATION.\***

**By W. W. Coblentz.**

[ABSTRACT.]

THE present investigation was undertaken for the purpose of obtaining measurements of the thermal radiation emitted from a planet as a result of warming of its surface by exposure to solar radiation, including heat radiated by virtue of a possible high internal temperature of the planet itself, and also selectively reflected solar radiation of long wave-lengths. It is shown that the latter is probably small and negligible in comparison with the radiation emitted as a result of heating by solar radiation.

By comparing the transmission of the direct solar radiation, through a 1-cm. cell of water, with the transmission of the radiation emanating from the planet, a measurement is obtained of the intensity of the planetary radiation.

Radiometric measurements were made on Venus, Mars, Jupiter, Saturn, and the Sun, and in cases where similar measurements had been made at Mt. Hamilton, California, in 1914, the data were found in good agreement.

The radiometric measurements of the water-cell transmissions of the radiations from Jupiter and from the Sun were practically

---

\*Scientific Paper No. 460, price ten cents.



the same indicating (1) that the outer atmosphere of Jupiter does not become sufficiently heated to emit long wave-length infra-red radiation, and (2) that any radiation emanating from its interior is entirely trapped by the surrounding atmosphere.

The intensity of the planetary radiation increases with decrease in the density of the surrounding atmosphere, and (as interpreted from the water-cell transmissions) in percentage of the total radiation emitted, is as follows: Jupiter (0), Venus (5), Saturn (15), Mars (39) and the Moon (80).

The intensity of the planetary radiation from the northern hemisphere of Mars was found to be less than from the southern hemisphere. This is to be expected in view of the observed cloudiness over the northern hemisphere which is approaching the winter season and hence is at a lower superficial temperature.

In Appendix I, measurements are given of the spectral energy distribution and the temperature of the sun as determined by means of a series of transmission screens placed in front of the stellar radiometer. The data obtained verify previous measurements indicating stellar temperatures ranging from  $3000^{\circ}$  K. for red, class-M stars, to  $12,000^{\circ}$  K. for blue, class-B stars.

---

#### COMPOSITION, PURIFICATION AND CERTAIN CONSTANTS OF AMMONIA.<sup>7</sup>

By E. C. McKelvy and C. S. Taylor.

[ABSTRACT.]

THE work presented in this paper forms a portion of that undertaken by the Bureau of Standards on the determination of the physical constants of materials used as refrigerating media, many of which have already been determined and published for ammonia, namely, specific heat of the liquid, latent heat of vaporization, specific volume of liquid, and vapor pressure. This paper deals mainly with the methods of purification and the tests for purity of the samples used in the determination of the various thermodynamical properties of ammonia, and gives assurance that the material used was of high purity.

An investigation was made of the composition and testing of commercial liquid ammonia. Analyses showed the presence of the following impurities: Non-condensing gases, water, pyridine,

---

<sup>7</sup> Scientific Paper, No. 465, price ten cents.



acetonitrile, ammonium acetate, and volatile materials containing carbon. Quantitative tests on eight standard American brands of commercial ammonia indicated the presence of less than 0.1 per cent. of impurities. Similar tests on three brands of German origin showed a somewhat larger percentage of impurities.

The best commercial samples were chosen as a starting point for further purification. It was found that water could be very completely removed from liquid ammonia by contact with metallic sodium in the form of fine wire. Numerous fractional distillations were found to remove most other impurities except the dissolved non-condensing gases. Difficulty was experienced in removing the latter gases, but by subliming the ammonia vapor into a container immersed in liquid air or by freezing the liquid into small crystals by its own evaporation, the content of non-condensing gas was found to be very materially reduced. Fifteen samples were prepared by five different methods for use in the physical measurements. Samples were prepared which contained: less than 0.003 per cent. by weight, of water, which was the limit of the chemical test applied; less than 1 part in 1,000,000, by volume, of non-condensing gases, and less than 0.01 per cent. of other impurities.

The density of solid ammonia was determined at  $-79$  and  $-185^{\circ}$  C., as 0.817 and 0.836 g./cm.<sup>3</sup>, respectively. The freezing point was found to be  $-77.70^{\circ}$  C., and the vapor pressure at that temperature, 45.2 mm. of mercury.

#### SPECIFIC VOLUME OF SATURATED AMMONIA VAPOR.<sup>s</sup>

By C. S. Cragoe, E. C. McKelvy and G. F. O'Connor.

[ABSTRACT.]

SEVERAL years ago the Bureau of Standards began the determination of the various thermodynamic properties of ammonia to establish an experimental basis for engineering tables to be used in the refrigerating industry. The present paper is the last of a series of papers on the determination of those properties under saturation conditions.

The specific volume, or the numerical reciprocal of density, of the saturated vapor was measured in the temperature interval  $-50$  to  $+50^{\circ}$  C. by two methods: One a direct method and the other

---

<sup>s</sup> Scientific Paper, No. 467, price five cents.



an optical method. Ammonia of high purity was used in all of the measurements.

The first method involved a direct determination of the mass of the vapor contained in a known volume, using three calibrated glass picnometers. Both phases, liquid and vapor, were present and in equilibrium. A correction was made for the mass of the liquid, using the results obtained from a separate determination of the specific volume of the liquid (already published). The vapor was superheated about  $0.1^{\circ}$  C. in order to prevent condensation taking place on the walls of the picnometers. The effect of adsorption was studied by introducing into the picnometers a large number of thin-walled glass tubes, thereby increasing the surface area about ten times. The results indicated that the effect of adsorption was no greater than the inherent inaccuracies of the method.

In the second method the refractive index  $n$  of the vapor was measured, using a Fizeau-Pulfrich interferometer, and the specific volume  $u'$  was calculated from the Gladstone and Dale relation,  $u'(n-1)=\text{constant}$ . The constant in this relation was determined from the mean of several measurements of the specific volume and refractive index of the vapor at  $0^{\circ}$  C. and 760 mm. pressure.

The specific volume was calculated at various temperatures by means of the Clapeyron equation,  $L = \theta(u' - u)dp/d\theta$ , using the experimental results previously obtained at this bureau for the latent heat of vaporization  $L$ , the specific volume of the liquid  $u$ , and the slope of the vapor-pressure temperature curve  $dp/d\theta$ . Above  $0^{\circ}$  C. the measurements by the two methods are in fair agreement with the calculated values, differing at most by about 0.3 per cent. At lower temperatures the results found by the direct method are systematically lower and those found by the optical method are systematically higher than the calculated values, amounting to about 2 per cent. at  $-50^{\circ}$  C. These systematic differences are believed to be due, in the direct method, to a thin film of liquid on the walls of the picnometers above the surface of the liquid, and to an adsorbed film of gas on the interferometer plates in the optical method.

Since the results by the two methods differ from the Clapeyron values in opposite directions and by about the same amount, the latter were chosen as the most probable values. The final results



are represented by the empirical equation  $\log_{10} u' = 1939.0331/\theta - 32.06611 + 10.704105 \log_{10} \theta + 0.0862366 \sqrt{406.1 - \theta} + 0.002667 (406.1 - \theta)$  in which  $u'$  is expressed in  $\text{cm.}^3/\text{g}$  and  $\theta$  in degrees absolute ( $^{\circ} \text{abs.} = ^{\circ} \text{C.} + 273.1$ ).

#### TENTATIVE STANDARD TEST METHODS AND PERCENTAGES OF OIL AND MOISTURE IN HAIR PRESS CLOTHS.<sup>9</sup>

By F. R. McGowan and C. W. Schoffstall.

[ABSTRACT.]

PRESS cloth is a heavy textile fabric usually 13 inches in width and ranging up to  $\frac{1}{2}$  inch in thickness. It is used in the oil-pressing industries in the presses for extracting the oil from the pulpy matter. Since it undergoes a pressure of approximately 2000 lb./in.<sup>2</sup>, a strong, resilient fibre is required, which makes it desirable to use hair fibres, such as camel hair, human hair, horse hair, or goat hair.

The material is bought on a weight basis so that the oil, which is added to permit the use of efficient manufacturing processes, and the moisture are important items. The methods are outlined for determining these percentages. The petroleum-ether method for extraction of oil is given. The sample is placed in a Soxhlet tube and extracted for five hours, after which the solvent is evaporated and the percentages are obtained. A means of distinguishing between the quantities of mineral and fatty oil is given. The method of obtaining moisture content is the usual one of obtaining weight as received and then drying and obtaining bone-dry weight.

The standards suggested are: Moisture, 11 per cent.; oil, 5 per cent.; water-soluble material,  $2\frac{1}{2}$  per cent.

#### SHELLAC.<sup>10</sup>

By Percy H. Walker and Lawrence L. Steele.

[ABSTRACT.]

A DESCRIPTION is given of the source, manufacture, uses and common methods of testing shellac. It is shown that the generally accepted iodine value method for determining rosin in flake shellac may be subject to very large errors, and this method can not be

<sup>9</sup> Technologic Paper, No. 231, price five cents.

<sup>10</sup> Technologic Paper, No. 232, price five cents.



applied to cut shellac. The amount of material soluble in a light petroleum distillate and the acid number of this material are shown to be quite constant for pure shellac, and a method of determining adulteration, both by rosin and other substances which can be as easily applied to cut shellac as to flake shellac, has been developed. Suggested specifications for pure orange flake shellac and orange shellac varnish are given.

---

**Properties of Rochelle Salt Related to the Piezo-electric Effect.** JOSEPH VALASEK. (*Phys. Rev.*, Dec., 1922.)—A rod of crystalline quartz cut in a certain manner develops on its two ends electrical charges of opposite kinds when it is stretched. Other crystals also exhibit this piezo-electric effect, but not too much is known about its cause. The recent development of a telephone based on this phenomenon makes it desirable to learn more. Rochelle salt, a double tartrate of sodium and potassium, shows the effect and shows it in such a manner as to present itself as a tempting mark for the experimenter, for an increase of temperature from  $-20^{\circ}$  to  $-10^{\circ}$  C. makes its piezo-electric modulus become more than five times as great as at the lower temperature, while an increase from  $20^{\circ}$  to  $30^{\circ}$  C. reduces the modulus from 8.1 to 1.08. The mode of attack was to vary the temperature and to study the corresponding changes in physical properties. No unusual type of variation was found in the cases of refractive index, thermal expansion, specific rotatory power of an aqueous solution and reversible electro-optic rotation. Speaking of the electrical resistance the author says: "Between  $-20^{\circ}$  and  $+30^{\circ}$  C., however, it was found to depend on the direction of the current, being only one-half as great in one direction as in the other at  $0^{\circ}$  and at  $20^{\circ}$ ." "In view of the fact that none of the properties measured show changes with temperature which correspond with those of the piezo-electric effect, it is probable that the elastic or piezo-optic constants must change in such a way as to account for the piezo-electric changes." G. F. S.

**Positive-ray Analysis of Potassium, Calcium and Zinc.** A. J. DEMPSTER. (*Phys. Rev.*, Dec., 1922.)—With slight improvements the method of his previous researches was used. Confirming Aston's results, potassium was found to have two isotopes of atomic weights 39 and 41, the intensity ratio of the two being about 18 to 1. This relation would give 39.1 for the mean atomic weight of ordinary potassium. Calcium gave two isotopes of atomic weights 40 and 44, the former being 70 times as strong as the latter. The four isotopes of zinc gave atomic weights of 64, 66, 68 and 70. The last of these appears in only a small quantity. G. F. S.



NOTES FROM THE RESEARCH LABORATORY,  
EASTMAN KODAK COMPANY.\*

THE SIZE-FREQUENCY DISTRIBUTION OF PARTICLES OF  
SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS  
AND ITS RELATION TO SENSITOMETRIC  
CHARACTERISTICS. III.<sup>1</sup>

By E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard.

AN improved method of studying microscopically the size-frequency distribution of silver halide in a photographic emulsion is given in detail, together with an estimate of the principal sources of error in the method. Frequency curves and data are given for a number of typical emulsions ranging from the slowest to the fastest. It has been found that an exponential equation of the form  $Y = Y_0 e^{-kx}$  fits some of the data very closely, while for other data another, a Gaussian equation of the form  $Y = Y_0 e^{-k(x-d)^2}$ , can be used to express the distribution of sizes,  $Y$  being the frequency per 1000 and  $x$  the size of the grains. The distribution of total area of grains in each case per unit area of plate, together with the variation in class size is more important photographically than the simple frequency distribution. It is obtained by multiplying each side of the above equation by the factor  $N/1000.X$ , in which  $N$  represents the total number of grains per square centimetre of the plate. Empirical sensitometric characteristics for these emulsions were also determined and are summarized in tabular form for comparison with the frequency data. The data show definitely that the relative speed of the emulsions increases rapidly with the increase of average size of the grains contained therein. Of the other characteristics, no definite statement can be made since these depend much more on the variation of other factors in the preparation and coating of the emulsions.

---

\* Communicated by the Director.

<sup>1</sup> Communication No. 148 from the Research Laboratory of the Eastman Kodak Company and published in *J. Phys. Chem.*, February, 1923, p. 141.



**THE SIZE-FREQUENCY DISTRIBUTION OF PARTICLES OF  
SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS  
AND ITS RELATION TO SENSITOMETRIC  
CHARACTERISTICS. IV.<sup>2</sup>**

By E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard.

THE existence of statistical variation of sensitivity among silver halide grains is discussed. For photolysis in a homogeneous system, a mathematical expression is developed relative to the density-exposure function and has the formula  $D' = -\ln[e^{-D_m} + (1 - e^{-D_m})e^{-k'I_0}]$ . The relation of statistical variation of inertia to the density-exposure function will correspond with the inertia-variation function. Conditions permitting this correspondence are noted. If the size-frequency corresponds with the sensitive-frequency then the curve of "reciprocity size-frequency" gives the inertia-variation curve; integration of this, the density-exposure function. For the most general case where  $dD/D_m - D = k'dE$  and  $k = f(i)$  or a function of inertia, the integration gives  $D = D_m (1 - e^{-\mu})$  where  $\mu = D_m/k'(1 - e^{-k'E})$ .  $E$  is the exposure and  $D_m$  the maximum density.

---

**AN INSTRUMENT (DENSITOMETER) FOR THE  
MEASUREMENT OF HIGH PHOTOGRAPHIC DENSITIES.<sup>3</sup>**

By Loyd A. Jones.

IN this paper a densitometer, designed for the measurement of very high densities, is described. In the earlier part of the paper the essential requirements of instruments of this type are considered and the principles used in some of the well-known instruments for this purpose are discussed. Following this a detailed description of the new instrument is given.

The high intensity of illumination on the density being measured is obtained by imaging, at a magnification of unity, the filament of a locomotive headlight lamp on the diffusing element in contact with which the sample is placed. The intensity of the

---

<sup>2</sup> Communication No. 153 from the Research Laboratory of the Eastman Kodak Company and published in *J. Phys. Chem.*, January, 1923, p. 1.

<sup>3</sup> Communication No. 160 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, March, 1923, p. 231.



comparison beam is controlled primarily by an adjustable sector shutter placed in a collimated beam of light between two elements of one of the lens combinations used to form an image of the light source on the comparison target. The photometric field is obtained by the use of the well-known Lummer-Brodhun cube. In addition to the adjustable sector diaphragm, a rotating sector disc is used for reducing the intensity of the comparison beam. Diaphragms consisting of perforated metal plates may also be introduced for control of the intensity. The adjustable sector diaphragm was calibrated on the photometer bar, utilizing the inverse square law as a means of varying the intensity in a known manner. The results show that the scale readings are directly proportional to the intensity to well within the photometric limit. While the previous instruments used for measuring density fail to produce satisfactory results on densities greater than 3.0, this instrument functions satisfactorily up to densities of 8.0. The sensitometric curve of a material exposed to X-rays was determined and found to be similar to the characteristic curves of the same material when exposed to white light except that the maximum density was found to be approximately 6.0 in the case of the X-ray exposure instead of 3.0 in the case of the exposure to white light.

---

#### PRELIMINARY NOTE ON THE SPECTRAL ENERGY SENSITIVITY OF PHOTOGRAPHIC MATERIALS.<sup>4</sup>

By Loyd A. Jones and A. L. Schoen.

THE paper contains an account of preliminary measurements made to determine the amount of energy of various wave-lengths required to produce a definite photographic effect. The radiation from a tungsten ribbon filament lamp was dispersed by means of a quartz monochromatic illuminator. The photographic plate (Seed 30) was exposed for a known time, the energy density at the exposing plane being measured by means of a high-sensitivity thermopile and galvanometer. The plate was then developed to a gamma of unity and the resultant density measured. From the data obtained, the energy density in ergs per square centimetre required to give a density of unity when developed to a gamma

---

<sup>4</sup>Communication No. 166 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Amer.*, March, 1923, p. 213.



of unity was computed for various wave-lengths. These values are also expressed in terms of quanta per square micron. These values (quanta per square micron) vary from 280 at  $\lambda = 460\mu\mu$  up to 450 at  $\lambda = 400\mu\mu$ .

---

**Analysis of the Energy Distribution in Speech.** I. B. CRANDALL and D. MACKENZIE. (*Bell System Tech. J.*, July, 1922.)—Of the making of applications of the vacuum tube amplifier there is truly no end. Here it is used to get the total energy record of the voice speaking a sentence and at the same time a second tube in a resonant circuit provides the energy record of a range of vibration frequencies existing in the same spoken sentence. By adjusting the latter circuit the energy contribution of each of twenty-three frequencies contained in the speech was obtained for four men and two women. The greatest energy for three of the men was found for frequencies near 150, while the maximum for the fourth was at about 500. The maxima for the women occurred, of course, at somewhat higher frequencies than for the three men. One woman's voice contained considerable energy in the component of frequency 2000. With this exception no frequency higher than 1300 contributed anything notable to the energy integral.

From another point of view these experiments are of interest in leading to this conclusion, "We may take 125 ergs per second as the total sound energy flow from the lips with the normally modulated voice." It thus becomes clear that a member of the Senate of the United States using this type of voice could filibuster for an entire day with the expenditure of less than a single foot-pound of energy.

G. F. S.

**The Theory of Probabilities Applied to Telephone Trunking Problems.** E. C. MOLINA. (*Bell System Tech. J.*, November, 1922.)—A number of problems in machine switching are solved. They can in general be reduced to equivalent problems in throwing dice. Some idea of the importance attached to this type of problem in practice may be inferred from the fact that a study was made of 100,000 calls in order to settle a point in question.

"Machine switching development, therefore, gave a great impetus to the application of the theory of probabilities to telephone engineering and in the Bell System work along this line has been in progress, systematically, for many years. The work has included not only the theoretical solution of many trunking problems, but has also involved the computation of special probability tables and collection of data by means of which theoretical results have been closely checked."

G. F. S.



## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

### COLLECTION AND EXAMINATION OF EXPLOSIVE DUSTS.<sup>1</sup>

By L. J. Trostel and H. W. Frevert.

[ABSTRACT.]

A METHOD devised for measuring the dustiness of air should prove of practical value in determining the presence of explosive mixtures of dust in grain elevators and certain industrial plants.

Briefly, the scheme is to filter a measured volume of dusty air through a paper thimble, either by a calibrated hand pump or by a small, portable electrically driven blower, equipped with a Venturi meter and manometer.

The following information can thus be secured: (a) Solids per cubic foot of air; (b) particle size and composition; and (c) in heavy dusts, the "relative flammability," a standard laboratory explosibility test.

The device can be used on all the ordinary explosive dusts and under practically all plant conditions.

### THE EFFECTS OF WATERPROOFING MATERIALS AND OUT-DOOR EXPOSURE UPON THE TENSILE STRENGTH OF COTTON YARN.<sup>2</sup>

By H. P. Holman and T. D. Jarrell.

[ABSTRACT.]

UNBLEACHED and unsized warp yarn, treated with various waterproofing materials, was tested to determine its tensile strength and then exposed to the weather. At the end of one year the treated yarn in most cases was stronger than the untreated yarn similarly exposed, but weaker than the treated yarn before being exposed. Yarn subjected to three treatments containing asphalt showed no material loss in tensile strength after being exposed. Raw drying oils caused more deterioration than the same oils previously boiled with metallic driers. In most cases, semi-drying and non-drying oils caused as much deterioration as raw-drying oils. The addition of burnt umber to a drying-oil treatment had a decided preservative effect.

---

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *J. Ind. Chem.*, **15** (March, 1923) : 232.

<sup>2</sup> Published in *J. Ind. Eng. Chem.*, **15** (March, 1923) : 236.



INDUSTRIAL MOLD ENZYMES.<sup>3</sup>

By Kokichi Oshima and Margaret B. Church.

[ABSTRACT.]

THE supposition that fungi produce extracellular and intracellular enzymes is accepted provisionally. The extracellular enzymes can be obtained by percolating mature fungi with water, but the latter cannot be obtained by mere treatment with water. Some investigators have tried to get the intracellular enzyme from koji residue, a mold ferment grown on a large scale on some substratum, and the whole washed free from extracellular enzymes, by treating with many solvents. Negative results were always obtained. Experiments show that extracellular and intracellular enzymes are the same, and after a certain period of growth all enzymes are excreted. Many investigators have shown the same results with other fungi. In the present investigation the work was quantitative, and the ratio of exo- and endo-enzymes during the cultivation of *A. oryzae* and *A. flavus* was found.

Soon after spore formation almost all enzymes have been excreted into the culture media. The increase and decrease of enzymes in the mycelium is quite rapid, but in the culture medium it is quite slow. It is doubtful whether the excretion of enzymes is due to the autolysis of the mycelium, because at the time of the most rapid excretion of enzymes the weight of mycelium is increasing and the maximum amount of exo-enzyme occurs simultaneously with the maximum quantity of mycelium. In experiments intended for the study of the influence of culture media, etc., on the production of mold enzymes, therefore, the estimation of the enzymes produced in the mycelium is an incorrect method of procedure, particularly when it is realized that through differences in culture media the rate of growth and the time of sporing may be varied.

---

**Power Losses in Insulating Materials.** E. T. HOCH. (*Bell System Tech. J.*, November, 1922.)—The author shows that in insulators the power loss is measured by the product of the phase difference by the dielectric constant. This product varies but little for good insulators over a large range of voltages and frequencies. Pyrex glass seems to have, of all materials investigated, the lowest power loss, while phenol fibre has the greatest. The change of the loss with temperature is very considerable. G. F. S.

---

<sup>3</sup> Published in *J. Ind. Eng. Chem.*, 15 (1922) : 1.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

### POWDERED COAL.

By John Blizard.

POWDERED coal has proved an economical fuel for steam raising, cement making, metallurgical furnaces, and many other purposes. For steam raising, with a properly constructed boiler and furnace, a continuous efficiency of over 80 per cent. may be maintained. For other purposes a high temperature with no regenerators may be maintained by using powdered coal, with less coal consumption than when using producer gas, stokers, or hand firing.

The unit system alone is economically applicable for small installations, where less than about ten tons a day are used.

For larger installations the multiple system, with Raymond or Fuller mills and with indirectly fired driers, seems to be preferable.

To distribute the coal, screw conveyers are recommended to convey large quantities of coal short distances, and either the Fuller-Kinyon pump or compressed air to convey it long distances.

The Quigley weighing tank is a valuable adjunct to the compressed air distribution.

The direct low-pressure system of distribution should be used solely to distribute coal short distances to small furnaces, where the cost and inconvenience of using separate bins and feeders for each furnace is unwarranted.

The foregoing summarizes the results of a study, made by the writer, of powdered coal plants in Canada and the United States. Further details are given in Bulletin 217 of the Bureau of Mines.

### THE CHLORIDE VOLATILIZATION PROCESS.

By Thomas Varley.

THE art of treating ores by the chloride volatilization process is still in the experimental stage. The process has not been sufficiently developed along metallurgical lines to warrant a definite statement as to the exact place it will occupy in the industry. The basic theory of the process has received the attention of prominent

---

\* Communicated by H. Foster Bain, Director.



metallurgists for twenty years, and considerable research and experimental work have been carried on.

If commercially utilized, the process will fill a long-felt want in metallurgy, especially in the treatment of oxidized and semi-oxidized or "carbonate" ores of copper, lead, and silver. Such ores are difficult to treat by gravity concentration or by flotation; in the former their tendency to slime upon crushing and their being of lower specific gravity than the sulphide minerals cause serious losses; in the latter much has been done in sulphidizing oxidized ores and subsequently recovering the artificial sulphides by flotation. Difficulties in proper sulphidizing and the low recoveries obtained have not balanced the cost of the treatment in many plants and in very few has it proved successful.

Evidently there is a big void to fill in the treatment of these ores. No radical changes in present methods are forecast, but it is obvious that chloride volatilization can have a distinct place as a method of treatment for ores that are not readily amenable to present methods. In many plants it might replace concentration methods, especially where part of the mineral content in the ores exists in forms other than sulphides.

Further details covering the experiments by the Bureau of Mines in coöperation with the University of Utah are given in Bulletin 211.

---

#### EFFECTS OF TEMPERATURE AND TIME OF DISTILLATION ON THE CRUDE OILS FROM OIL SHALE.

By Lewis C. Karrick.

THE amount and quality of oil that can be produced from any shale may be made to vary to an important degree by changing the temperature relations existing in the shale charge during destructive distillation. The rate at which the oil is formed from the shale is affected by the rate of heat supply, and therefore by the temperature of the shale during its thermal decomposition. The quality of the oil formed may be controlled by altering the temperature of the shale, and, therefore, the rate of formation of the oil. Variations in the yield and quality of shale oils may be caused by inherent properties of the retort used, but in any event the properties of the crude oil and yield are very largely the result of the extent to which the thermal decomposition has progressed.



Recognition of these principles will aid in explaining to a large degree the reasons for the wide variations in oils produced from the same shales by different "processes." These principles also may be applied in the operation of different types of retorts in order that crude oils of a type most profitable to the operator may be produced.

The Bureau of Mines has conducted an extended series of tests in the destructive distillation of oil shales, in order to determine the wide variations that may be effected in the quality and yield of shale oil by changing the rate and temperature at which the oil is formed. These tests furnished interesting information on the four related points: Yield of oil, quality of oil, temperatures required to distill shales, and time required for distillation.

The principal conclusions from these tests are:

(1) They indicate that the changes in the quality of crude shale oils, produced by varying the rate of distillation, may be due to (a) the temperature at which the decomposition took place, and (b) the extent to which the thermal reaction progressed.

(2) The temperature studies show conclusively that the oils produced in the slow rates of distillation are actually produced at much lower temperatures than the oils formed by rapid distillation.

(3) The practical limits to which controlled cracking within the retort may be carried are not yet determined, but since time or temperature are such important factors in the production of good crude shale oils, it should be feasible in commercial retort design to balance size of retort and heating surface, rate of heat supply to the shale, size of shale particles, and rate of throughput, so that the most desirable rate of distillation, and subsequent thermal reactions, can be obtained. Thus, it should be possible to govern, within fairly wide limits, the qualities of the crude oils obtained, and thereby to produce crude oils of the most desirable properties for commercial needs.

(4) Data of the nature presented in the curves, when obtained from similar tests made on other shales, will furnish a logical basis of comparing different shales.

Further details will be found in Serial 2456 of the Bureau of Mines.



**Acoustic Wave Filters.** G. W. STEWART. (*Phys. Rev.*, December, 1922.)—Filters for light and for electric waves are known. Why, one wonders, have sound filters been so long delayed? It is true that Helmholtz resonators act as filters when the small opening is placed at the ear, but it has remained for this eminent investigator in the field of acoustics to investigate the theory of sound filters and to devise filters that embody his results. He has made and tested three kinds of filters. "The low frequency pass filter will give approximately zero transmission at all frequencies above, and fairly good transmission below a certain predetermined frequency. The high frequency filter will transmit above a minimum frequency. The single-band filter will transmit a group of frequencies. . . . In these filters, the cutoffs are not sharp and the performances are not exactly as just stated."

"Low frequency pass filters were made, for example, by two concentric cylinders joined by walls equally spaced and perpendicular to the axis. Each chamber thus formed had a row of apertures in the inner cylinder which served as the transmission tube. In one case the volume of each chamber was 6.5 cm.<sup>3</sup>; the radius of the inner tube, 1.2 cm.; the length between apertures, 1.6 cm. A chamber and one such length of inner tube is called a section. Four such sections were found to transmit 90 per cent. of the sound from zero to approximately 3200 d.v. where the attenuation became very high, resulting in zero transmission up to 4600 d.v. where transmission again appeared." There is manifestly an error in the printed article, for, where the author gives 90 per cent., as just quoted, the table of results gives but .9 per cent.

The filtering action of such sections is ascribed to interference. It is suggested that the filters will be found to have applications, not only in the laboratory but in connection with the phonograph and in wireless telephony, with the megaphone and loud-speaking devices. The design of musical instruments may later be affected. "In wireless telegraphy an acoustic filter makes possible the simultaneous reception of an indefinite number of messages with the same antenna."

G. F. S.

**The Range of Alpha-particles from Polonium in Various Gases.** C. W. VAN DER MERWE, University of Cape Town. (*Phil. Mag.*, Feb., 1923.)—The range was determined by C. T. R. Wilson's method of photographing the tracks caused by the particles in damp air suddenly expanded. In moist air at normal temperature and pressure the range was found to be 3.59 cm., whereas Geiger found it to be 3.58 cm. by a different method. The range in hydrogen is 16.28 cm. and in methyl bromide only 1.76. In all the cases examined there is a close agreement of the ranges of the particles from polonium with similar determinations made by Bragg using radium A and radium B as sources of the rays. A fine series of ten photographs of the tracks is appended.

G. F. S.



# THE FRANKLIN INSTITUTE.

---

(*Proceedings of the Stated Meeting held Wednesday, April 18, 1923.*)

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, April 18, 1923.

MR. W. C. L. EGLIN, Vice-president, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of :

H. D. Arnold, Esq., Ph.D., Research Engineer, Western Electric Company,  
463 West Street, New York City, New York.

Charles A. D. Burk, Esq., B.S., Inventor, Atlantic City, New Jersey.

Miss Marion Reilly, A.B., 2015 DeLancey Place, Philadelphia, Pennsylvania.

Charles Burton Thwing, Esq., Ph.D., Physicist, 3339 Lancaster Avenue,  
Philadelphia, Pennsylvania.

W. W. Trench, Esq., Assistant Secretary, General Electric Company, Schenectady, New York ;

lectures before the Sections as follows :

" Radiation and Chemical Reaction " by

Herbert S. Harned, Ph.D.,

Assistant Professor of Chemistry,

University of Pennsylvania,

Philadelphia, Pennsylvania ;

" Physical Measurements of Audition and Their Bearing Upon the Theory  
of Hearing " by

Harvey Fletcher, Ph.D.,

Research Laboratory,

American Telephone and Telegraph Company and

Western Electric Company, Incorporated,

New York City, New York ;

" The Theory of Light and Vision " by

James P. C. Southall, A.M.,

Professor of Physics,

Columbia University,

New York City, New York ;

and a lecture before the Stated Meeting, March 21, 1923, by

Harvey C. Hayes, Ph.D.,

Research Physicist,

U. S. Navy,

on " Measuring Ocean Depths by Acoustical Methods " :

a course of lectures on

" The Electron in Chemistry " by

Sir Joseph John Thomson, O.M., F.R.S., LL.D., Ph.D., D.Sc.,

Master of Trinity College,

Cambridge, England.



on the afternoons of April 9th to 13th, inclusive; also the following additions to the library, 103 bound volumes, 12 unbound volumes, 75 pamphlets and 2 drawings.

The Chairman then announced that the next business of the meeting would be the presentation of the awards made by the Institute on recommendation of its Committee on Science and the Arts and recognized Mr. W. H. Fulweiler, who introduced Dr. Albert W. Hull, to whom was awarded the Howard N. Potts Medal for his paper on "The Crystal Structure of the Common Elements" which appeared in the JOURNAL of the Institute for February, 1922. Mr. Fulweiler said:

"Mr. Chairman, Members of the Institute, Ladies and Gentlemen: Following its custom, your Committee on Science and the Arts has reviewed all of the papers published in the JOURNAL of the Institute during the year 1922 with a view to determining whether any of these papers possess such special merit as would warrant recognition by the Institute.

"As a result of such an inquiry, your Committee has selected the paper entitled 'The Crystal Structure of the Common Elements,' by Dr. A. W. Hull of the Research Laboratory of the General Electric Company, this paper appearing in the February number of the JOURNAL for 1922, as being of such special character as to be worthy of the Howard N. Potts Medal.

"This medal is the highest award available to the Committee and is given for papers of the first importance that have appeared in the JOURNAL of the Institute. In his paper, Doctor Hull has recorded the results of research that has extended over a number of years.

"As is well known, the investigation of the crystal structure involves the use of X-rays and Doctor Hull has not only developed a new method of attack—the powder method which gives at a single exposure the reflection from all possible crystal faces—but has also developed apparatus which enables the observations to be made almost automatically, thus greatly conserving the operator's time and attention.

"Doctor Hull also made very valuable suggestions as to methods of interpreting the observations. This subject is still so new that aside from its great theoretical interest, the practical applications are as yet undeveloped. It will undoubtedly find application in the study of alloys, in the failure of metals under stress and the study of the magnetic properties of ferrous metals.

"Mr. Chairman, I have the honour to present to you Albert Wallace Hull, Doctor of Philosophy, of the Research Laboratory of the General Electric Company of Schenectady, New York, to receive from you the Howard N. Potts Medal for his paper on 'The Crystal Structure of the Common Elements.'"

The Chairman presented the Medal and Certificate to Doctor Hull, who thanked the Institute for the high honour conferred upon him.

Mr. Fulweiler was again recognized and described the universal measuring machine made by the Société Genevoise d'Instruments de Physique, to whom had been awarded the Edward Longstreth Medal. He said:

"Mr. Chairman, Members of the Institute, Ladies and Gentlemen: It seems particularly appropriate that The Franklin Institute Devoted to Science and the Mechanic Arts and located in Philadelphia, workshop of the world, should give recognition to the perfection of apparatus that is of fundamental importance in the control of precision in manufacturing operations.



"After a careful and thorough investigation, your Committee on Science and the Arts has recommended the award of the Edward Longstreth Medal to the Geneva Society of Geneva, Switzerland, for its universal measuring machine. This medal is awarded for particularly meritorious improvements and developments in machines and mechanical processes.

"The increasing demand for accuracy in manufacturing machines and machine parts calls for precision in workmanship and this depends not only upon the skill of the workman, but also upon the accuracy and invariability of measuring apparatus used in the process of manufacture.

"Until recently, the micron, one-thousandth of a millimetre or about one-half of one ten-thousandth of an inch, has been considered as useful only in scientific measurements. To-day it has become a practical unit of measurement in those industries where the very highest degree of accuracy is required.

"Practical measurements depend upon the use of standard and limit gauges and in order that these measurements may be accurate, it is essential that the gauges should be of the proper size when made and that suitable means shall be available in order to determine that these dimensions are retained. This naturally requires the development of accurate standard means for making these measurements, and it is for such a purpose that the apparatus that is the subject of this award, which is known as the Universal Measuring Machine, has been devised.

"The Universal Measuring Machine was developed by the Geneva Society for the purpose of furnishing a machine by means of which it is possible to determine absolute lengths of a gauge or piece of work to within one-millionth of an inch. A variety of auxiliary apparatus is provided whereby either internal or external measurements may be made and also the necessary chucks, etc., which permit the measuring of the pitch of screw threads.

"Your Committee has made a series of tests to verify the accuracy of the main screw thread of this instrument by referring to the ultimate physical standard of length, that is, the wave-length of monochromatic light. These experiments were made with a Fabry and Perot interferometer and the results verify the very high degree of accuracy claimed for the apparatus by the Geneva Society.

"Mr. Chairman, I have the honour to present to you Mr. Roy Y. Ferner, the American Representative of the Geneva Society of Geneva, Switzerland, to receive from you on their behalf the Edward Longstreth Medal."

The Chairman presented the Medal, Certificate and Report to Mr. Ferner, who said:

"As the American Representative of the Société Genevoise d'Instruments de Physique, I am sure of their appreciation of the honour conferred upon them in the bestowal of these evidences of recognition of the value of their work in the development of this Universal Measuring Machine. The honour is of added significance in that the Société Genevoise, a company having many years' experience in the manufacture of scientific apparatus, is honoured by this for the development of a machine adapted to the needs of production manufacturing—in particular, for providing means for the direct reference of all measuring equipment used in a manufacturing plant to one standard of length, thus securing greater uniformity and accuracy in products which are dependent upon length measurements.



"The practical application of the exact sciences to the needs of industry must accompany development in science. It is for this that The Franklin Institute stands. In this instance we see the application of several researches of the International Bureau of Weights and Measures. The encouragement of such developments by these awards of your Institute is very valuable. They benefit industry, they give added zest to the researches of the scientist, and they reward the medium of the application of these researches to industry. On behalf of the Société Genevoise d'Instruments de Physique, I thank you."

The paper of the evening on "The Cathode-ray Oscillograph and Its Application to the Exact Measurement of Explosion Pressures, Potential Changes in Vacuum Tubes, and Magnetos" was then presented by D. A. Keys, Ph.D., Department of Physics, McGill University, Montreal, Canada. A description was given of the special form of cathode-ray oscillograph devised during the war by Sir J. J. Thomson, O.M., for use in conjunction with the piezo-electric properties of crystals to measure the very rapid and large variations of pressure due to an explosion in water. The method consists in placing in the water near the explosion, a special form of crystal detector which transforms the pressure variations into corresponding changes in electrical charge by virtue of the piezo-electric properties of the crystals. These electrical variations act upon a beam of moving electrons which are magnetically controlled in the oscillograph, and this beam falling directly on a photographic plate traces out the time-pressure history of the explosion. The arrangement is thus a pressure recording device of negligible inertia and is the only method known of determining exactly the maximum pressure in water produced by an explosion of gun-cotton, T. N. T. or other high explosive. With this form of oscillograph changes which take place in one fifty-thousandth of a second have been measured. Among the many possible applications of this instrument to physical and engineering investigations, mention was made of recent work on the rise of potential in vacuum tubes at the beginning of the discharge. The same scheme may be used in the study of specific heats of gases at high temperatures and in the investigation of the characteristics of a magneto.

The subject was illustrated by lantern slides and experiments.

After a discussion, a rising vote of thanks was extended to the speaker.

Adjourned.

R. B. OWENS,  
*Secretary.*

---

## COMMITTEE ON SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday, April 4, 1923.)*

HALL OF THE INSTITUTE,  
PHILADELPHIA, April 4, 1923.

MR. W. H. FULWEILER *in the Chair.*

The following report was presented for final action:

No. 2798: Way Adjustable Hinge.

The following reports were presented for first reading:

No. 2797: Merrill Process of Industrial Heating by Oil Circulation.

No. 2805: Ives' Photometric and Radiometric Researches.

R. B. OWENS,  
*Secretary.*



## SECTIONS.

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, March 1, 1923, at eight o'clock, with Dr. George A. Hoadley in the Chair. The minutes of the previous meeting were read and approved.

Edwin F. Northrup, Ph.D., member of the Institute, delivered a lecture on "High Temperature Investigation," in which a description was given of the methods and technic used in the study of matter at high temperature, free from chemical contamination.

The paper, which was illustrated by means of lantern slides and an ironless induction furnace, was discussed at length; a vote of thanks was extended to Doctor Northrup; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, March 8th, at eight o'clock, with Dr. Thomas D. Cope in the Chair.

The paper of the evening on "Ionization and Resonance Phenomena" was presented by Dr. Charles B. Bazzoni, Professor of Experimental Physics, University of Pennsylvania, Philadelphia, Pa. The speaker pointed out that the modern theories of atomic structure in which the properties of materials are related to the grouping of electrons in the atoms are to a large extent checked experimentally by determinations of ionization and resonance potentials. These quantities are intimately connected with the structure and stability of the atoms and with the production of the ordinary optical spectra.

The speaker also outlined briefly the development of the dynamic theories of atomic constitution including recent refinements. Certain experimental methods used to investigate the stability of the atomic and molecular systems were described and discussed, and finally the way in which the production of spectral series depends upon the electronic arrangements was brought out. A non-technical statement of the state of our knowledge in this rapidly changing field was made by the lecturer. The subject was illustrated by lantern slides.

After a brief discussion, a rising vote of thanks was extended to Doctor Bazzoni. Adjourned.

T. R. PARRISH,  
*Acting Secretary.*

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, March 15, 1923, at eight o'clock, with Dr. H. J. M. Creighton in the Chair. The minutes of the previous meeting were read and approved.

Herbert S. Harned, Ph.D., Assistant Professor of Physical Chemistry in the University of Pennsylvania, delivered an address on "Radiation and Chemical Reaction." The photochemical nature of all chemical reactions was discussed from the viewpoint of mathematics



The communication was discussed; a vote of thanks was tendered to Doctor Harned; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

*Section of Physics and Chemistry.*—A meeting of the Section was held in the Hall of the Institute on Thursday evening, March 29, 1923, at eight o'clock, with Dr. James Barnes in the Chair. The minutes of the previous meeting were read and approved.

Harvey Fletcher, Ph.D., Research Laboratories of the American Telephone and Telegraph Company and the Western Electric Company, Incorporated, New York City, delivered a lecture upon "Physical Measurements of Audition and Their Bearing upon the Theory of Hearing." A comprehensive summary was given of the results obtained by the use of the vacuum tube and high-quality telephone transmitters and receivers in making measurements in audition.

The communication was discussed at length; a vote of thanks was extended to Doctor Fletcher; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

---

## THOMSON LECTURES.

SIR JOSEPH JOHN THOMSON, O.M., F.R.S., LL.D., Ph.D., D.Sc., Franklin Medallist, Honorary Member of the Institute, Master of Trinity College, Cambridge, England, delivered a series of lectures on "The Electron in Chemistry" in the Hall of the Institute on the afternoons of April 9th to 13th, inclusive.

The first lecture was delivered on the afternoon of April 9th at 3.30 o'clock. Dr. Walton Clark, President of the Institute, welcomed Sir Joseph and Mr. W. C. L. Eglin, Vice-president of the Institute and member of its Board of Managers, presided. The following is a brief synopsis:

The atomic theory had little effect on the progress of chemistry as long as nothing was known about the structure of the atom. The discovery of the electron showed that atoms have a structure and gave a clue to its character. The arrangement of the electrons in the atom. Number of electrons in the atom. Electronic isomers. Active nitrogen. Instability of configuration when electrons are too crowded. Eight the maximum number of electrons which can be on the outer layer of an uncharged atom. This result involved a periodicity in the properties of the atoms of the different elements such as is expressed by Mendeleef. Periodic law. Valency. The size of atoms. Specific inductive capacity. Work required to abstract an electron from an atom. Methods for testing the configuration of electrons in an atom.

Dr. Arthur L. Day, Director, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., M.F.I., presided at the second lecture on Tuesday, April 10th. Attention was given to the following:

The combination of atoms to form molecules. Physical interpretation of chemical "bonds." Double bonds. Union of two similar atoms to form a molecule. Union of two or more dissimilar atoms. "Positive and negative" valencies. Arrangement of electrons in octets. Comparison with the results of



the old valency rules. Stability of systems of octets. Instability chains of octets in general. Stability of  $\text{CH}_2$  chains. Polar molecules. Importance of these in chemical reactions. Problem of the water molecules. Arrangement of the electrons in chlorides, chlorates, perchlorates, carbonates, sulphates, sulphites, nitrates, nitrites. Connection between the arrangement of the electrons and the acidic or basic properties of the compound.

Dr. A. A. Noyes, Director of Chemical Research, California Institute of Technology, Pasadena, California, presided at the third lecture on Wednesday, April 11th. Special attention was given to the following.

Mechanism of chemical combination. Active molecules. Their occurrence in such reactions as the combination of hydrogen with chlorine or of oxygen with hydrogen. Afford a physical basis for Thiele's theory of partial valencies. "Molecular compounds." "Residual affinity." Double salts. Electron theory gives a physical basis for Werner's coördination theory. Mechanism of electrolytic dissociation. Structure of the ions in liquids. Catalytic action. Variable valency and homologous elements.

Dr. Joseph S. Ames, Director of the Physical Laboratory, The Johns Hopkins University, Baltimore, Maryland, M.F.I., presided at the fourth lecture given on Thursday, April 12th. The following topics were considered:

Connection between variable valency and the magnetic properties of the elements. Magnetism of chemical compounds. Magnetism of oxygen. Diamagnetism affords a method of checking the configuration of the atom and the migration of the electrons in chemical combination. The electron theory of solids. General considerations. Calculation of the energy of a solid.

The closing lecture of the series was given on Friday afternoon, April 13th. Dr. Augustus Trowbridge, Professor of Physics, Princeton University, Princeton, New Jersey, M.F.I., presided. The following topics were considered:

The calculation of the electron theory of the compressibility of the elements in a solid state. Critical periods of vibration for solids. Latent heat of evaporation. Compressibility and specific inductive capacity of salts. The structure of metals, salts and insulators. Electrical conductivity of metals.

Individuals and groups, physicists and chemists, from the research laboratories of the great electrical manufacturing and electricity supply companies and from institutions of learning from nearly every state of the Union and Canada were in attendance.

---

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, April 18, 1923.)*

#### HONORARY MEMBERS.

GENERAL G. FERRIÉ, Inspecteur des Services de la Telegraphie, Militaire et des Transmissions, 51 bis, Boulevard Latour-Maubourg, Paris, France.

DR. A. A. MICHELSON, Department of Physics, University of Chicago, Chicago, Illinois.



## RESIDENT MEMBERS.

MISS MARION REILLY, 2015 DeLancey Place, Philadelphia, Pennsylvania.

DR. CHARLES BURTON THWING, 3339 Lancaster Avenue, Philadelphia, Pennsylvania.

## NON-RESIDENT.

DR. H. D. ARNOLD, Engineering Department, Western Electric Company, New York City, New York.

MR. CHARLES A. D. BURK, Atlantic City, New Jersey.

MR. W. W. TRENCH, The General Electric Company, Schenectady, New York.

## CHANGES OF ADDRESS.

MR. C. P. BOWER, 11 Eastern Avenue, Wyndmoor, Montgomery County, Pennsylvania.

MR. FRANK H. BREWSTER, 118 Bedford Avenue, Buffalo, New York.

MR. WILLIAM J. BURGESS, 940 South 55th Street, Philadelphia, Pennsylvania.

MR. BENJ. J. DASHIELL, Dunkirk P. O., Calvert County, Maryland.

MR. JOHN M. HAMMOND, 14 East Abington Avenue, Chestnut Hill, Philadelphia, Pennsylvania.

MR. ALLEN HAZEN, 23 West Forty-third Street, New York City, New York.

MR. ERNST JOHANSEN, New England Oil Refining Company, Fall River, Massachusetts.

MR. FRANK H. STEWART, 4416 North Fifteenth Street, Philadelphia, Pennsylvania.

MR. FRANK M. TAIT, Callahan Bank Building, Dayton, Ohio.

---

**NECROLOGY.**

Sir James Dewar, The Royal Institution, London, W. I., England.

MR. R. C. M. HASTINGS, The International Telephone Company, Columbus, Ohio.

MR. A. B. STITZER, Republic Engineers, Inc., 60 Broadway, New York City, New York.

---

**LIBRARY NOTES.****PURCHASES.**

American Electrochemical Society—Transactions, 1921. 1922.

BACON, R. F., and HAMOR, W. A.—American Fuels, Ed. 1, 2 vols. 1922.

CAIN, J. C.—Manufacture of Dyes. 1922.

CLAYTON, W.—The Theory of Emulsions and Emulsification. 1923.

COOKE, T., AND SONS, LTD.—Adjustment and Testing of Telescope Objectives 1921.

GILDEMEISTER, E.—Volatile Oils, vol. 3. 1922.

GLAZEBROOK, SIR RICHARD—Dictionary of Applied Physics, vol. 3. 1923.

HAMILTON, H.—Scientific Treatise on Smoke Abatement. 1917.

PARTINGTON, J. R., and PARKER, L. H.—Nitrogen Industry. 1923.



Royal Society of London—Catalogue of Scientific Papers, vols. 16-17.  
1918, 1921.

STRUBEN, A. M. A.—Tidal Power. 1921.

Tables Annuelles de Constantes et Données Numériques 1913-16, 2 vols.  
1921-22.

Who's Who. 1923.

Year Book of Wireless Telegraphy and Telephony. 1922.

#### GIFTS.

Aldrich Pump Company, Aldrich Pumps. Allentown, Pennsylvania, 1922.  
(From the Company.)

Alexander Milburn Company, Catalogue of Carbide Lights. Baltimore,  
Maryland, 1921. (From the Company.)

Alfred University, Catalogue 1922-23. Alfred, New York. (From the  
University.)

Allis-Chalmers Manufacturing Company, Electrically Driven Saw Mills.  
Milwaukee, Wisconsin, 1922. (From the Company.)

Alloy Welding Processes, Limited, Bulletins 32, 38, 40 and 42. London,  
England, no date. (From the Company.)

American Sheet and Tin Plate Company, Pamphlets on Corrosion of Steel and  
Copper. Pittsburgh, Pennsylvania, no date. (From the Company.)

American Woolen Company, List of Woolen Mills and Pamphlet, "From Wool  
to Cloth." Boston, Massachusetts, 1921. (From the Company.)

Amherst College, Catalogue 1922-23. Amherst, Massachusetts. (From the  
College.)

Atlas-Imperial Engine Company, Incorporated, Catalogue 22, Atlas-Imperial  
Diesel Engines. Oakland, California, 1922. (From the Company.)

Beaumont, R. H., Company, Bulletin 61, Beaumont Skip Hoist for All Bulk  
Materials. Philadelphia, Pennsylvania, 1922. (From the Company.)

Bridgeport Brass Company, Bulletin No. 15, Brass Pipe and Piping. Bridge-  
port, Connecticut. (From the Company.)

British Thomson-Houston Company, Limited, Electric Drive in Textile Mills.  
Rugby, England, 1922. (From the Company.)

Brooke Tool Manufacturing Company, Limited, Brooke Engineers Small Tools,  
1920. Birmingham, England, 1920. (From the Company.)

Brown Hoisting Machinery Company, Catalogue L, Drop-forged Chain for  
Conveyors and Elevators. Cleveland, Ohio, 1922. (From the Company.)

Buffalo Forge Company, Catalogues Nos. 205, 700 and 800. Buffalo, New  
York, 1922. (From the Company.)

Cadman, A. W., Manufacturing Company, Catalogue of Valves. Pittsburgh  
Pennsylvania, no date. (From the Company.)

Cameragraph Company, The Book of Cameragraph. Kansas City, Missouri,  
1922. (From the Company.)

Canada Department of Mines, Thirty-first Annual Report and Bulletin No. 6,  
Irrigation Practice and Water Requirements for Crops in Alberta. Ottawa,  
Canada, 1922. (From the Department.)

Carling Turbine Blower Company, Carling Turbine Blower Bulletin No. 50.  
Worcester, Massachusetts, 1922. (From the Company.)



- Carnegie Institution of Washington, Year Book No. 1. Washington, District of Columbia, 1922. (From the Institution.)
- Carpenter, P., A Companion to the Improved Phantasmagoria Lantern. London, England, 1835. (From Mr. John J. L. Houston.)
- Chase Companies, Incorporated, Chase Condenser Tubes. Cleveland, Ohio, 1922. (From the Corporation.)
- City Parks Association of Philadelphia, Thirty-third Annual Report. Philadelphia, Pennsylvania, 1921. (From the Association.)
- Cole, Marchent and Morley, Limited, Pamphlets Nos. 70, 69, 66 and Catalogue No. 56 of Tram Cars and Brakes. Bradford, England, no date. (From the Company.)
- College of the City of New York, Catalogue 1922-23. New York City, New York. (From the College.)
- Columbia College, Catalogue 1921-22. Dubuque, Iowa. (From the College.)
- Columbia Machine Works, Catalogue of the Works, 1892 to 1922. New York City, New York, 1922. (From the Works.)
- Columbia University, Catalogue 1922-23. New York City, New York. (From the University.)
- Concordia College, Catalogue 1921-22. Moorhead, Minnesota. (From the College.)
- Copper and Brass Research Association, To Make a Good Car Better. New York City, New York, no date. (From the Association.)
- Crescent Machine Company, Crescent Wood-working Machinery. Leetonia, Ohio, 1922. (From the Company.)
- Crescent Tool Company, Catalogue No. 14. Jamestown, New York. (From the Company.)
- Cutter Company, Decreasing Production Interruptions. Philadelphia, Pennsylvania, no date. (From the Company.)
- Dartmouth College, Catalogue 1922-23. Hanover, New Hampshire. (From the College.)
- Franklin College, Catalogue 1922-23. Franklin, Indiana. (From the College.)
- Furman University, Catalogue 1922-23. Greenville, South Carolina. (From the University.)
- Georgetown University, Catalogue of College of Arts and Sciences, 1922-23. Washington, District of Columbia. (From the University.)
- Glasgow Electrical Engineering Company, Limited, Natural Power Electricity from the Wind. Glasgow, Scotland, no date. (From the Company.)
- Gwynnes Engineering Company, Limited, Suction Dredgers. London, England, no date. (From the Company.)
- Harper, A., Sons and Bean, Ltd., Machine Tools. Dudley, England, 1923. (From the Company.)
- Hillsdale College, Catalogue 1921-22. Hillsdale, Michigan. (From the College.)
- Horseley Bridge and Engineering Company, Limited, A Century of Progress. Tipton, Staffordshire, England, 1922. (From the Company.)
- Institution of Mining and Metallurgy, Transactions, 1920-21. London, England, 1921. (From the Institution.)



- Jenson and Nicholson, Limited, Electrical Insulating Varnishes, Enamels. London, England, 1922. (From the Company.)
- Kansas State Geological Survey, Bulletins 7 and 8. Lawrence, Kansas, 1921. (From the State Geologist.)
- Keystone Telephone Company, Booklet on Automatic Telephones. Philadelphia, Pennsylvania, no date. (From the Company.)
- Kobert Machine Company, Incorporated, How Electric Riveting was Made Commercial. New York City, New York, no date. (From the Company.)
- Ladd, George T., Company, Bulletins 20 and 21 of Water Tube Boilers. Pittsburgh, Pennsylvania, no date. (From the Company.)
- Lang, John, and Sons, Limited, Catalogue of Lathes and Booklet, Lang Surfacing and Boring Lathe. Johnstone, Scotland, 1922. (From the Company.)
- Leeds Electrical Construction Company, Limited, "Losles" Automatic Temperature Controller. Leeds, England, no date. (From the Company.)
- Library of Congress, Report of the Librarian of Congress and Report of the Superintendent of the Library Building and Grounds. Washington, District of Columbia, 1922. (From the Librarian.)
- Louis Allis Company, Bulletin No. 406, L-A Motors. Milwaukee, Wisconsin, no date. (From the Company.)
- Lumen Bearing Company, Hand-book for Engineers and Machine Designers. Youngstown, Ohio, no date. (From the Company.)
- Manchester Steam Users' Association, Memorandum by Chief Engineer for the Year 1921. Manchester, England, 1922. (From the Association.)
- Marquette University, Catalogue 1922-23. Milwaukee, Wisconsin. (From the University.)
- Massachusetts Institute of Technology, Directory of Officers and Students, 1922-23. Cambridge, Massachusetts, 1922. (From the Institute.)
- McGill University, Catalogue 1922. Montreal, Canada. (From the University.)
- Michell Bearings, Limited, Michell Viscometer. Newcastle-on-Tyne, England, no date. (From the Company.)
- Morris, Herbert, Incorporated, Morris Hoists, Book 5031. Buffalo, New York, 1923. (From the Corporation.)
- National Gas Engine Company, Limited, Booklets of Gas Engines, Oil Engines and Gas Plants. Ashton-under-Lyne, England, 1922. (From the Company.)
- Nevada Department of Mines, Annual Reports for 1910, 1913-14, 1915-16 and 1917-18. Carson City, Nevada. (From the Department.)
- New South Wales Department of Mines, Mineral Resources Note No. 31, Bulletin No. 1 and Records of the Survey. Sydney, New South Wales, 1921 and 1922. (From the Department.)
- New York University, Catalogue 1922-1923. University Heights, New York. (From the University.)
- Niagara Machine and Tool Works, Bulletin No. 51. Buffalo, New York, 1923. (From the Works.)
- Nicholson, Peter, The Student's Instructor. New York City, New York, 1837. (From Mr. John J. L. Houston.)
- VOL. 195. No. 1169—50



## BOOK REVIEWS.

THE ORIGIN OF SPECTRA. By Paul D. Foote and F. L. Mahler, Physicists, U. S. Bureau of Standards (American Chemical Society Monograph Series). 250 pages, illustrations, plates, 8vo. New York, Chemical Catalog Company, Inc., 1922. Price, \$4.50.

By a judicious mixture of classical mechanics and the quantum theory Bohr in 1913 proposed a very illuminating and suggestive explanation of the Balmer, Lyman and Paschen series in the spectrum of hydrogen. Since then Bohr with many co-workers has developed the theory to explain many other properties of the other elements besides hydrogen. In this field of work the authors of this book have contributed a large amount of valuable experimental work especially with regard to the ionizing and resonance potentials of the elements.

The book is divided into eleven chapters, namely, The Quantum Theory of Spectroscopy, Energy Diagrams, Ionization and Resonance Potentials for the Elements, Line Absorption Spectra of Atoms, Line Emission Spectra of Atoms, Cumulative Ionization, Thermal Excitation, Thermochemical Relations, X-ray Spectra, Photo-electric Effect in Vapors, Determination of  $h$  involving Line Spectra.

It is impossible to give short concise statements of the many important observations discussed in these chapters and the writer accordingly strongly recommends the book to chemists and physicists who are interested in the structure and mechanics of the atoms of the different elements.

The authors of the book are to be complimented on having presented such a comprehensive and suggestive survey of this modern field of investigation which, no doubt, will be the foundation for future developments in theoretical and practical physical chemistry.

JAMES BARNES.

INDEX GENERALIS (1822-23). General Year-book of the Universities. Published under the direction of R. de Montessus de Ballore, D.Sc., Professor in the Faculty of Sciences of Paris. 12mo, 2110 pages, paper bound. Paris, Gauthier-Villars et Cie. 50 Francs, net.

This work is intended to occupy the field that has long been occupied by the German "Minerva," the "Handbuch der gelehrten Welt." The war interrupted the publication of that work, and while it has now resumed issue, the French competitor has developed to a very large and comprehensive volume. The copy of the French publication now in hand is intended for English-speaking persons, but the general text is in French, and some portions of the specific descriptions are in the language of the country in which the institution is located. It would perhaps be better if the whole was in French. The vast majority of those who consult this work are able to read the text in that language, but business considerations must, of course, not be disregarded, especially in a work involving such expense. The value of such a work depends entirely upon the thoroughness with which the material has been gleaned and arranged. The present edition, a great improvement on the first, seems to have been carefully prepared and to cover all the necessary data. A glance



over its pages shows the enormous extension of school and college teaching and the vast array of men and women who are devoted to educational service. The book is well printed in clear, though necessarily small, type. It will be of great use in library work and the educational field.

HENRY LEFFMANN.

**PRACTICAL PHYSIOLOGICAL CHEMISTRY**, by Philip B. Hawk, M.S., Ph.D. Eighth edition, revised, 8vo, xvi-666 pages, index, two full-page plates in color, four additional full-page plates and 197 figures of which twelve are in colors. Philadelphia, P. Blakiston's Son and Company. \$5 net.

Little is needed concerning this book, except to chronicle the appearance of the new edition, as it has been so long before the public and been received with great favor. In this edition introduction of new matter has compelled an increase of bulk, although some matter—become antiquated—has been deleted. The additions relate chiefly to blood, acidosis, quantitative analysis of urine, vitamins and determination of kidney function. The author directs special attention to Benedict's test for sugar and Folin's test for albumin, quantitative procedures that have been set forth in an addendum. It is believed that these mark a very important advance in the available procedures in urinary analysis. Acknowledgment is made to several persons who aided the author in this revision. It is interesting to compare this large octavo volume with the thin duodecimo books on clinical chemistry which fifty years ago sufficed as guide for the hospital laboratory—when there was one!

HENRY LEFFMANN.

**INDUSTRIAL ORGANIC CHEMISTRY**. By Samuel P. Sadtler, Ph.D., LL.D., and Louis J. Matos, Ph.D. Fifth edition, revised, enlarged and partly rewritten. xvi-667 pages, index and 141 illustrations, 8vo. Philadelphia, J. B. Lippincott Company, 1923. \$8 net.

The first edition of this work was issued in 1891, when it promptly assumed a leading place in the field to which it was devoted. Treating comprehensively the wide field of applied organic chemistry, its popularity enabled the author to issue in comparatively rapid succession, revised editions, which was a great advantage in a book devoted to a department in which accumulation of data and modifications of methods were proceeding actively. The work has, therefore, been kept up to date. In the present edition, Doctor Sadtler has had the assistance of Doctor Matos, who has taken care of the chapters on textile fibres, coal-tar industries, bleaching and dyeing. These chapters involve much detail of the war-time chemistry, and the developments of that period have necessitated rewriting most of the text. The major portion of the book has been revised by the senior author. In his field, a large amount of new matter has been introduced in consequence of the enormous development of the industries relating to cellulose and its derivatives, and also the newer methods concerning fatty oils, especially the hydrogenation problems. The sections on statistics that have heretofore been included in the book have been dropped, as it is held that the U. S. Government reports furnish all the data required.

Chemical industries have taken an enormous development of late in English-speaking countries, on account of the problems arising out of the World War,



and a comprehensive work of this character, brought as this is up to date, will be of great value to the work-chemist. The mechanical execution of the book is excellent.

HENRY LEFFMANN.

GENERAL SCIENCE, WITH EXPERIMENT AND PROJECT STUDIES. By George A. Bowden, B.S., University of Cincinnati. 622 pages, index and 334 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. \$1.68 net.

This book has somewhat larger scope than most of the works on general science that have appeared of late. The popularizing of science by means of lectures, journals and books has been going on for a number of years, gaining in volume and comprehensiveness each year. The object of science is the discovery of truth, and in strict construction of this definition, it is not necessary that the discovery should inure to the advantage of mankind, indeed, it may be said that some of the most recent striking applications of science have resulted in disadvantages. It is a question whether high explosives, asphyxiating gases, submarines and airplanes have not done more harm than good, and many would incline to put the automobile in the same category.

This book is intended to meet the modern demand for education along what may be termed practical lines. The swing of the educational curriculum from the old system in which the classics, mathematics, logic and homiletics dominated, has given curricula dominated by natural and physical sciences, vocational training, and the study of the relations of the human-being to the environment. Whether this transition will be of substantial advantage time alone will show, but teachers are not lacking who feel that pupils are being over-laboratoried and that a partial return to the drill methods of the older courses will be beneficial. The author states frankly that his book has been written to aid in bringing the student into direct contact with natural phenomena and objects that have real significance in life. In fact, he emphatically states the theme is "life" and particularly human life. A brief note on the development of the human race from its earliest period opens the book. It is doubtful if archeologists would endorse all the statements. Our knowledge of prehistoric man is very scanty, and it is unwise to set forth a series of statements in a dogmatic form, leading the student to believe that the data are established. In this preliminary note no account is taken of the extraordinary ability of drawing and painting attained by the cavemen in certain parts of Europe. The origin of language is also a problem of great difficulty. The book takes up the origin of the art of making fire and gives illustrations of the means used by existing savage peoples for making fire. An interesting account is given of the old tinder box, flint and steel, and an outline of the development of the manufacture of matches. In the paragraph on the use of phosphorus in matches, the word, by a curious typographic error, is six times spelled "phosphorous." Taking up the chemistry of fire, the preparation and properties of oxygen are described, but the directions are not at all commendable. No information is given as to the chemical change that occurs in heating the oxygen mixture, nor any suggestion as to the part that the manganese dioxide plays. It is true that the exact nature of this action is not known, but the student



should be informed of the reason for its addition. The student is directed to fill five bottles with oxygen, but is not told how much potassium chlorate to take to obtain a given volume of gas. The manner of mounting the test-tube is quite objectionable, and the pneumatic trough is merely academic, as no support for the collecting bottle is shown. At the present day when excellent illustrations of apparatus for experiments are available, such rude drawings are ridiculous. At the end of each section suggestions for practical problems are given under the title "Projects."

The book covers a wide field, much attention being given to hygienic problems. It is very liberally illustrated, mostly with creditable pictures but a few of those in the earlier portion are inferior. The text is interspersed with many questions, and the demonstrations are mainly adapted to classes provided with apparatus, for which reason one is more puzzled at the awkward arrangement of the apparatus for making oxygen. Taken all in all, however, a great deal of scientific information may be gathered from the book, and much useful advice concerning the problems of daily life will be found in it. The mechanical execution is good, and there is a fair index.

HENRY LEFFMANN.

ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS. By Victor von Richter. Edited by R. Anschütz and H. Meerwein. Vol. 3, heterocyclic compounds. Translated from the eleventh German edition, by E. E. Fournier D'Albe. xviii-310 pages and index. Philadelphia, P. Blakiston's Son and Company. Price, \$6 net.

The appearance of the second volume of this work was noted less than a year ago, and what was then said will apply equally to the present volume. The book written by Victor von Richter many years ago reached a high degree of popularity in a short time and has since maintained its position. The original text has been kept up to date by the industry of Anschütz who, in the later period, has been assisted by Meerwein. The third volume completes the translation. Each of the three volumes has a separate index. These have been prepared with great care and it is probable that they are much superior to the indexes of the original, as it is generally known that Continental authors are not strong on indexing. The Germans, however, are doing a great deal better of late years than the French. The book contains an immense amount of matter well arranged and well displayed, and the immensity of the field of organic chemistry is well shown by an examination of the three volumes. It may be worth while considering whether the sub-title "Chemistry of the Carbon Compounds" is now necessary.

HENRY LEFFMANN.

ULTRA-VIOLET RADIATION: ITS PROPERTIES, PRODUCTION, MEASUREMENT AND APPLICATIONS. By M. Luckiesh, Director of Applied Science, Nela Laboratories. 8vo, 249 pages, index and 12 plates. New York, D. Van Nostrand Company.

Here one may find interesting news from "outer darkness." Those rays, too rapid for our eyes to utilize, constitute one of the most attractive fields of study in physics. In the preface we are told that about one hundred and twenty years have elapsed since the discovery that the visible spectrum is but a small section of the range of vibrations. That the rainbow is due to some



action of the raindrops on light was surmised by Greek scientists, but knowing nothing of the composition of white light, no explanation of the phenomenon could be furnished. Newton's experiment, conducted with a beam of light of appreciable size, gave him a series of overlapping spectra, in which not only were the color distinctions more or less obliterated, but the dark spaces in the solar spectra were unseen. Wollaston observed these, but the mapping of the few very conspicuous ones was done by Fraunhofer, whose name is indissolubly attached to the series. Many years passed before the ultra-violet and infra-red rays were detected. Scheele in 1777 came very near detecting the former, but it was not until 1800 that Sir William Herschel observed the existence of infra-red radiations, and one year later, Ritter detected the ultra-violet. Much more attention seems to be paid to the study of ultra-violet rays than to the infra-red. This may be due to the much greater activity of the former. It was long known that the violet end of the spectrum is most active chemically both on inorganic matters and living tissues, and this gives a strong incentive to investigation, but the susceptibility of the standard photographic emulsions to these rays affords an easy means of determining the range and line spectrum of them. Wood has shown some interesting actions of infra-red, having among other effects discovered that when trees in full leaf are photographed through filters excluding all other rays, the leaves appear as if covered with snow. In the recent work of Palmer on plant pigments, mention is made of a practical application of the discovery that the green pigment of plants has a different emission relation from ordinary green paints, so that the painted canvas, intended to deceive aviators, could by means of light filters be distinguished from real foliage.

The book in hand contains a very large amount of information on that portion of "invisible light" that has shorter wave-lengths than can be appreciated by the human eye. We do not know whether any of the lower animals have a greater range, and it is useless to speculate upon the problem. One of the most striking features of the shorter wave-lengths is the stoppage of them by some common materials quite transparent to ordinary light. Glass, mica, celluloid and gelatin are of this nature. Quartz and fluorspar are different, transmitting a considerable portion of ultra-violet light freely, and thin films of the cellulose acetate, which is now used for certain classes of picture-film also seem to interpose but little resistance to those rays not far above the violet. The title of the book "Ultra-violet Radiation" is better than "Ultra-violet Light," although the latter is most usual. Ordinary humanity limits the word "light" to the form of energy that affects the human eye in a specific manner, just as "sound" is understood as referring to a class of waves that specifically affect the human ear. In both cases waves exist of similar nature to those respectively seen and heard, but not perceived by us. It may be laid down as a fundamental principle that if there were no eyes there would be no light, and if there were no ears there would be no sound. Light and sound, in the fundamental significance of those terms, are dependent on specific perception by certain sense organs.

Very little unfavorable criticism is developed in examining the book, but the tables of symbols for indicating the wave-lengths deserve some animadversion. There seems to be no reason for adopting  $m$  for  $\mu$ . The latter arrangement has gone into general use, and the welter of units and symbols that has



been caused by the rapid progress in chemistry and physics, should lead the scientific world to say "anathema" to anyone who introduces an unnecessary datum or sign. Nor can the author escape disapproval for allowing the fact that the publisher wanted to economize, justify the use of  $A^\circ$  for the correct method of writing the symbol of the unit now so largely used in expressing wave-lengths. It seems to the reviewer that it will be much better to drop the umlaut sign altogether, rather than attempt to retain it in a highly inaccurate and even misleading manner. " $A^\circ$ " means really "A degrees."

The book opens up a fascinating field of optics and the author has not only sifted the literature with care and thoroughness, but his own contributions to this and other departments of the science have been numerous and valuable. It is to be hoped that he will soon give us a book treating of the dark region at the other end of the spectrum. The work is a monograph and not an elementary text-book and we cannot expect, therefore, to have the apparatus and phenomena set forth in great detail, but in view of the interesting developments of the applications of these radiations, their powerful effects, especially on protoplasm, more space given to the description of the forms of apparatus now available for producing the rays and employing them would have been welcome, but after all the lists of dealers in the apparatus will probably afford sufficient information to those who having general experience in optics wish to enter upon work in this special field. The chapter on the action of the radiations upon living matter is of special interest to the biologist and clinician.

HENRY LEFFMANN.

### PUBLICATIONS RECEIVED.

*Institute for Government Research.* Service monographs of the United States Government, No. 9. The Weather Bureau, its History, Activities and Organization, by Gustavus A. Weber. 87 pages, 8vo. Baltimore, The Johns Hopkins Press, 1922. Price, \$1.

*The Riddle of the Rhine, Chemical Strategy in Peace and War.* An account of the critical struggle for power and for decisive war initiative. The campaign fostered by the great Rhine factories, and the pressing problems which they represent. A matter of preëminent public interest concerning the sincerity of disarmament, the future of warfare, and the stability of peace, by Victor Lefebure, with a preface by Marshal Foch, and an introduction by Field-Marshal Sir Henry Wilson. 282 pages, plates, 8vo. New York, E. P. Dutton and Company, 1923. Price, \$2.

*Géométrie Descriptive*, par Gaspard Monge. Augmentée d'une Théorie des Ombres et de la Perspective. Extraite des papier de l'auteur par Barnabé Brisson. 2 vols, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1922. Price, 6 Francs.

*American Engineering Standards Committee.* Year Book, 1923. 48 pages, quarto. New York, Committee.

*Les Théories de la Relativité dépassant les Données de l'Expérience*, par le lieutenant-colonel corps. 43 pages, quarto. Paris, Gauthier-Villars et Cie., 1923. Price, 3 Francs 50.

*Cours de Mécanique Céleste*, par M. H. Andoyer. Tome I. 439 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 50 Francs.



*The Association of British Chemical Manufacturers.* Official directory of members with classified list of their manufactures. 319 pages, 8vo. London, Association, 1923. Price, 10 shillings, 6 pence.

*Plant Physiology*, by Vladimir I. Palladin. Authorized English edition edited by Burton Edward Livingston. Second American edition with a biographic note and chapter summaries by the editor. 360 pages, illustrations, portrait, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$4.

*Metals and Their Alloys.* A modern practical work dealing with metals from their origin to their useful application . . . by Charles Vickers. Partly based on the third edition of "Metallic Alloys," by William T. Brannt. 767 pages, illustrations, 8vo. New York, Henry Carey Baird and Company, Incorporated, 1923. Price, \$7.50.

*Interior Wiring and Systems for Electric Light and Power Service.* A manual of practice for electrical workers, contractors, architects and schools, by Arthur L. Cook. Second edition, thoroughly revised. 458 pages, illustrations, plates, 16mo. New York, John Wiley and Sons, Incorporated, 1923. Price, \$3.

*Institute for Government Research.* Service monographs of the United States Government, No. 17. The Federal Power Commission, its History, Activities and Organization, by Milton Conover. Baltimore, The Johns Hopkins Press, 1923. Price, \$1.

*Institut International de Physique Solvay. Atomes et Electrons.* Rapports et discussions du Conseil de Physique tenu a Bruxelles du 1er au 6 Avril 1921 sous les auspices de l'Institut. Publiés par la Commission administrative de l'Institut et MM les Secrétaires du Conseil. 271 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 20 Francs.

*Ontario Department of Mines: Thirtieth Annual Report* being volume xxx, part I, 1921. 197 pages, illustrations, plates, 8vo. Toronto (Canada), King's Printer, 1922.

*National Advisory Committee for Aeronautics: Technical Notes* No. 127, The Air Propeller, Its Strength and Correct Shape, by H. Dietsius. 9 pages, plates, quarto. No. 128, Tests on an Airplane Model AEG D1 of the Allgemeine Elektrizitäts Gesellschaft, A.-G., Airplane Construction Section. Conducted at the Göttingen Model testing laboratory for aerodynamics, by Max Munk and Wilhelm Molthan. 26 pages, plates, quarto. No. 130, Model Supports and Their Effect on the Results of Wind-tunnel Tests, by David L. Bacon. 8 pages, plates, quarto. No. 131, Variation in the Number of Revolutions of Air Propellers, by W. Achenbach. 7 pages, quarto. Washington, Committee, 1923.

*General Science with Experimental and Project Studies*, by Garfield A. Bowen. 634 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1923. Price \$1.68.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



# Journal of The Franklin Institute

Devoted to Science and the Mechanic Arts

Vol. 195

JUNE, 1923

No. 6

## THE ELECTRON IN CHEMISTRY.\*†

BY

SIR JOSEPH JOHN THOMSON, O.M., F.R.S., LL.D., Ph.D., D.Sc.

Master of Trinity College, Cambridge, England;  
Franklin Medallist, Honorary Member of the Institute.

### THE COMBINATION OF ATOMS TO FORM MOLECULES.

WE shall begin by considering molecules in the gaseous state, where each molecule is separated so far from its neighbours that it may be regarded as an individual and not as merely forming a brick in a much larger structure. Indeed, the term molecule when applied to the solid state is quite ambiguous without further definition; for example, from many points of view we can consider quite legitimately the whole of a large crystal as forming a single molecule. It is natural to expect that when the atoms are crowded together as in a solid, where each atom may come under the influence of a large number of neighbours, the arrangement of the electrons relatively to the atom may differ substantially from that in a gaseous molecule.

Let us begin with the simplest case, that of the union of two similar atoms each containing one electron. We see that if the atoms and electrons are arranged as in Fig. 2, where *A* and *B* are the atoms and  $\alpha$  and  $\beta$  the electrons, the mutual repulsion of the electrons may be balanced by the attraction of the positive charges on the electrons; and the mutual repulsions of the similarly electri-

\* A series of lectures given before The Franklin Institute, April 9-13, 1923.

† Continued from the May, 1923, issue, p. 620.

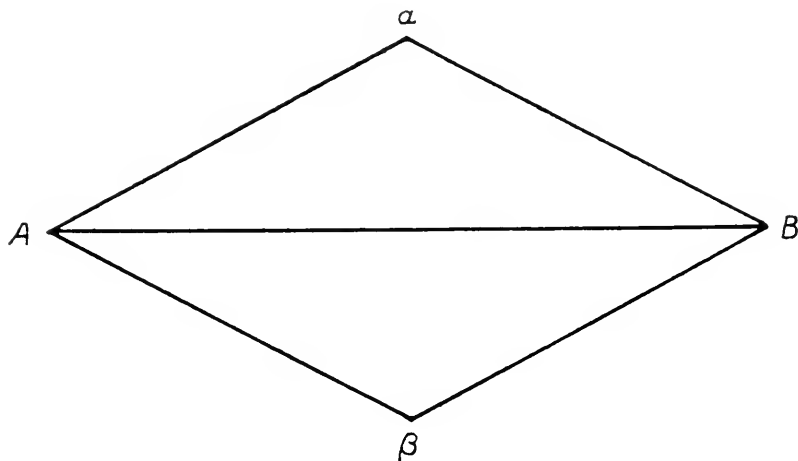
(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1923, by THE FRANKLIN INSTITUTE.



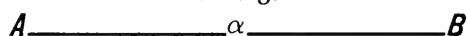
fied atoms by the attractions of the electrons. Thus we may regard the electrons in the atom as acting like hooks by which one atom gets coupled up with another. As the atoms are held together by the attraction of the pair of electrons  $\alpha, \beta$ , the presence of two electrons between the atoms may be taken as the physical interpretation of what is called a bond by chemists. In

FIG. 2.



this example and in general, two electrons go to each bond. There are, however, cases such as that of a positively electrified molecule of hydrogen (so frequently detected in positive-ray photographs) where a single electron is able to bind two atoms together. The arrangement being that represented in Fig. 3.

FIG. 3.



The dimensions and shape of the parallelogram represented in Fig. 2 will depend on the law of force between two positive charges at atomic distances as well as upon that between a positive charge and an electron. If  $e^2 \varphi\left(\frac{c}{r}\right)$  is the attraction between a positive charge  $e$  and an electron with equal charge separated by a distance  $r$  and  $e^2 \psi\left(\frac{c^1}{r}\right)$  the repulsion between two positive charges at a distance  $r$ , then if  $A\alpha = r$  and  $\angle A\alpha\beta = \vartheta$ , we have for equilibrium

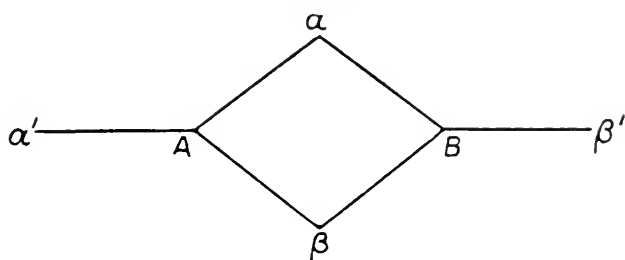
$$\begin{aligned} 2e^2\varphi\left(\frac{c}{r}\right)\cos\vartheta &= \frac{e^2}{4r^2\cos^2\vartheta} \\ 2e^2\varphi\left(\frac{c}{r}\right)\sin\vartheta &= e^2\psi\left(\frac{c^1}{2r\sin\vartheta}\right) \end{aligned} \quad (25)$$



Though the distance of an electron from its atom will obviously be not quite the same in the molecule as in the atom, we should expect that the differences would not be very large. For if they were, work would have to be done at some stage in the act of combination comparable with that required to ionise an atom, as this work is much greater than the equivalent of the heat developed by the union of the atoms to form a molecule we could not expect atoms under these conditions to combine to form molecules except in the presence of a very efficient catalyst.

Let us now pass to the case where each of the atoms contains two electrons. If only one pair of electrons is used up in uniting

FIG. 4.



the atoms, the arrangement would be that represented in Fig. 4, where the Greek letters represent the electron. In the language of chemists this would be expressed by saying that the atoms were united by a single bond and the molecule would be expressed by the formula  $-A-B-$ . The electrons  $\alpha'$  and  $\beta'$  would enable this molecule to link up with other molecules so that it would not be saturated. If, however, all four electrons are used in coupling up the atom, they will be at the corners of a square bisecting  $AB$  at right angles.

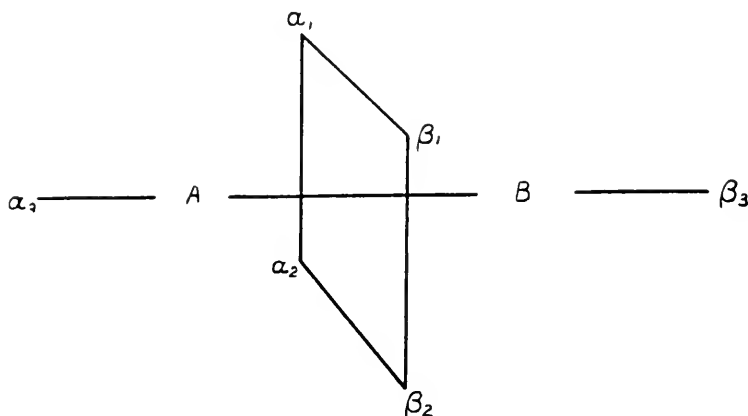
The system of four electrons instead of two between the positively electrified atom may be regarded as the physical equivalent of what the chemists call a double bond. Inasmuch as the equilibrium of four electrons in one plane, when their displacements are not confined to that plane, requires very strong restoring forces to make it stable, we should not expect the double bond to be permanent when the positive charges which exert the restoring force are as small as in this case, where their sum is only equal to the sum of the charges on the four electrons.

For the union of two tri-electron atoms, if all the electrons were used to couple up the atoms, there would be a hexagonal ring



of electrons in a plane bisecting  $AB$  at right angles, as this ring requires a greater positive charge than that of three units on each side to keep it in stable equilibrium it would be unstable. The most probable arrangement of the electrons is the octahedral one shown in Fig. 5 with four electrons between the atoms and two on the line  $AB$ ; this would be represented symbolically by

FIG. 5.

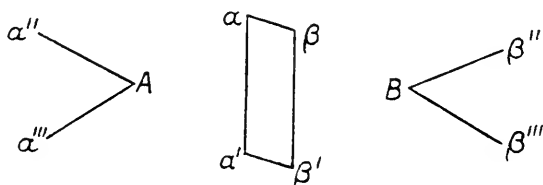


the formula  $-A = B-$ . The end electrons would enable it to bind other atoms so that the molecule would not be saturated.

#### FOUR-ELECTRON ATOMS.

These may form a molecule in which the electrons are as represented in Fig. 6, four electrons are between  $AB$  and the other four form two pairs beyond the extremities of the line  $AB$ .

FIG. 6.

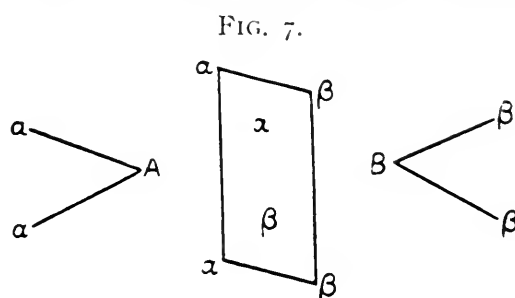


A peculiarity of the arrangement in Fig. 6 is that the molecule has four free electrons the same as the original atom, thus other atoms can be coupled up with the molecule, and we might have a chain of atoms, each atom being at the centre of a parallelepiped of eight electrons. We can show that a long chain of such atoms would be unstable, but it is evident that the four-electron atom is one peculiarly suited for forming



complexes containing several atoms. The carbon atom has four electrons in its outer layer and thus carbon atoms would have a great tendency to unite with each other. It is this tendency that is responsible for the Science of Organic Chemistry. I may point out in passing that we can obtain from the study of positive rays direct evidence of the coalescence of carbon atoms. For on a positive-ray photograph of benzene I found lines corresponding to  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ , where  $C_1$  represents a carbon atom;  $C_2$ , a carbon molecule;  $C_3$ , a carbon triplet, and so on.

The form we have suggested for the electrons in the molecule of atoms of this type is represented symbolically by the formula



$= A = B =$ . When we come to the case of five-electron atoms we have to introduce new considerations. We have seen that eight is the maximum number of electrons which can be in stable equilibrium in a single layer under the action of positive charges whose aggregate cannot exceed the total charges carried by the electrons. With a five-electron atom we have ten electrons in the molecule, while the aggregate positive charge, in the molecule, is also ten, which is not sufficient to keep the ten electrons in stable equilibrium if spread over a single layer. A simple way of arranging the electrons is shown in Fig. 7. Midway between the positive charges are six electrons which keep the atoms together, four of them at the corners of a square forming the normal double bond, while two others are inside the square.

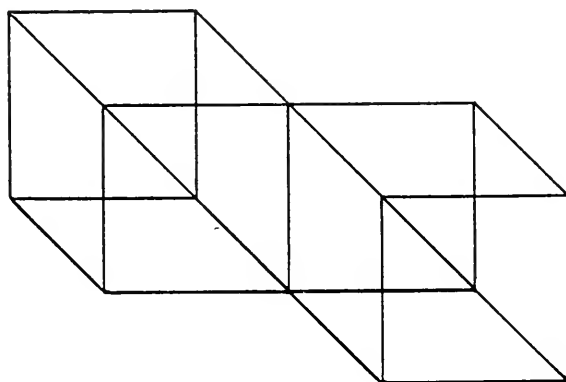
The remaining four electrons are arranged in pairs beyond the atoms  $A$ ,  $B$ , respectively. Thus we have eight electrons surrounding two atoms and two electrons. The arrangement is somewhat like that suggested for the carbon molecule with the addition of two electrons near the centre of the molecule.

When each of the atoms contains six electrons the arrangement is as follows: There are four electrons forming the normal double bond between the atoms, and two other sets of four, one



set beyond *A*, the other beyond *B*. Thus each of the two atoms may be regarded as being inside an octet of electrons, the two octets having four electrons in common. When each of the atoms contains seven electrons, we have fourteen electrons at our disposal. These may be arranged so that two of them form a single bond between the atoms while the remainder complete two octets with two electrons common to both, as is represented in Fig. 8. This, though a very symmetrical arrangement, is not the only conceivable one. For when the positive charges are large, as they are in this case, they might hold four or even more elec-

FIG. 8.



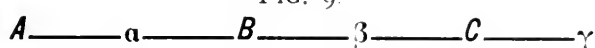
trons in stable equilibrium, even though the electrons were very close together. Thus suppose there were a double instead of a single bond between the atoms, this would account for four electrons, leaving ten to be distributed outside. If these were distributed symmetrically, there would be five around each atom, so that each atom would be the centre of a layer containing nine electrons, four coming from the double bond and five from those left over after the double bond has been provided for. Now nine electrons could not be in equilibrium if equally distributed under a central charge of seven, but if four of them are held close together in stable equilibrium under two positive charges, it is possible that there may be room for the other five to be so far apart that they can be kept in stable equilibrium by a positive charge of seven units.

It will be noticed that the molecules formed by the union of two atoms, each of which contains less than five electrons, have free electrons which are available for linking up with other mole-



cules. The one-electron atoms could form chains as in Fig. 9. Thus the process of aggregation is not exhausted by the formation of the molecule; these molecules will form further aggregations and thus tend to get into the solid or liquid state. On the other hand, the molecules formed by atoms with five or more electrons form saturated systems and will not tend to aggregate further. This agrees with the properties of the elements; for Li, Be, Bo, and C, whose atoms contain less than five electrons, are solids, while N, O, F and Ne, whose atoms contain five or more electrons, are gases.

FIG. 9.



From the consideration of the arrangements of the electrons in different molecules, we see that for the atoms containing four and five electrons we can regard the electrons in the molecule as roughly distributed over a single layer not very far from spherical, when, however, we reach the six-electron atom the electrons in the molecule form two cells, and a surface which would contain them all would have to be very elongated. We get some confirmation of this result from the study of the scattering of polarised light by gases. The theory of such scattering shows that the light scattered by a single electron in a direction at right angles to the incident beam is completely polarised and can be extinguished by a Nicol prism. The same thing is true when the light is scattered by a perfectly symmetrical body such as a sphere. If the scattering body is not perfectly symmetrical, if, for example, it is elliptical instead of spherical, the scattered light is never completely polarised and therefore cannot be entirely quenched by a Nicol. The ratio of the minimum to the maximum intensity of the light seen through a Nicol would be zero for a spherical body, but would be finite for an ellipsoid and would increase with the ellipticity. The value of this ratio may be taken as an indication of the deviation of the scattering body from sphericity. The scattering of light by molecules is due to the electrons in the molecules; we should expect that an arrangement of electrons in one shell would approach more closely to the spherical arrangement than an arrangement in two cells, and that two cells would approximate to the spherical more closely than three. Thus the



ratio of the minimum to the maximum intensity of the scattered light should increase with the number of cells. Lord Rayleigh<sup>8</sup> has determined the value of this ratio for several gases with the results given in the following table:

Gas.	Ratio Expressed as a Percentage.
Argon .....	.46
Hydrogen .....	3.83
Nitrogen .....	4.06
Oxygen .....	9.4
Carbon Dioxide .....	11.7
Nitrous Oxide .....	15.4

We see how small this ratio is for the symmetrical distribution of electrons round the argon atom. A striking feature of the table is the great jump between nitrogen and oxygen. We have seen that the passage from nitrogen to oxygen corresponds to the transition from an arrangement of the electrons in one cell to one in two cells, and thus involves a great loss in symmetry. The electrons in carbon dioxide and nitrous oxide require three cells for their arrangement and thus are less symmetrical than those in the oxygen molecule.

#### COMBINATION OF DIFFERENT ELEMENTS, CHEMICAL COMPOUNDS.

We may apply considerations similar to those we used to explain the formation of molecules of an element by the union of two similar atoms to the union of two different atoms to form the molecule of a compound.

Let us consider, for example, the union of a seven-electron atom with a one-electron atom. Suppose that  $A$  is the centre of the first atom,  $B$  that of the second.

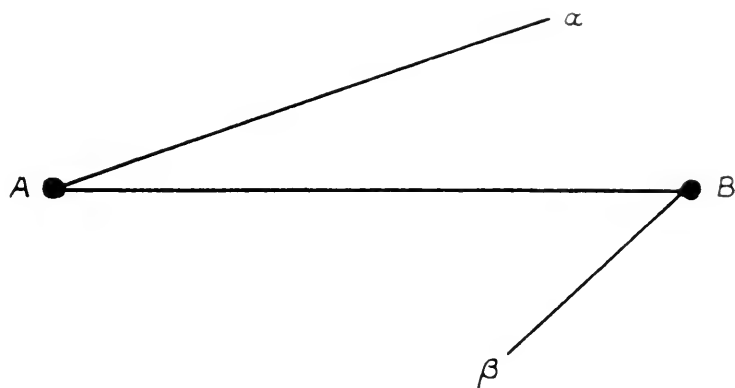
Let  $\alpha$  be an electron in the first atom,  $\beta$  one on the second. Then if  $B$  and  $\beta$  place themselves somewhat as in the figure, the attractions the two electrons exert on  $A$ ,  $B$  may keep these together in spite of their mutual repulsions, while the electrons are kept in equilibrium by the attraction upon them of the atoms  $A$  and  $B$ . The addition of  $\beta$  to the seven electrons already round  $A$  will raise the number in the outer layer of  $A$  to eight. Now suppose we attempt to attach another atom  $\beta'$  to  $A$ , this would introduce another electron into the outer layer round  $A$ , raising the number

<sup>8</sup> *Proc. Roy. Soc.*, 98, p. 57.



in this layer to nine. We have seen, however, that nine electrons in one layer cannot be kept in stable equilibrium by a positive charge of nine units; in this case nine units are all we have at our disposal and two of these are outside the layer. The outside ones will make the arrangement of electrons more stable than it would be in their absence. They will not, however, increase the stability more than they would if they were inside, and even in that case they could not make the arrangement stable. Thus  $A$  cannot hold

FIG. 10.



a second atom of the type  $B$ , so that the compound  $AB_2$  is impossible and that represented by  $AB$  is saturated. Thus, if  $B$  with its one electron is taken as the type of a monovalent atom, like hydrogen,  $A$  with its seven electrons would also be monovalent, and would in this respect act like fluorine. The electrons in the molecule  $HF$  would form a layer round the centre of the fluorine atom with the positive part of the hydrogen atom outside. Let us now suppose that  $A$  is a six instead of a seven-electron atom and let an atom of  $B$  get attached to it in the way we have supposed. This will raise the number of electrons in the layer round  $A$  to seven, so another atom can be attached before the number of electrons in the outer layer is raised to eight and the limit of stability reached. Thus  $A$  could form the unsaturated compound  $AB$  and the saturated one,  $AB_2$ , but  $A$  could not combine with more than two atoms of  $B$ . Thus  $A$  with its six electrons would behave like the atom of a divalent element, say oxygen.

In a similar way we see that if  $A$  contained five electrons it would form the unsaturated compounds  $AB$  and  $AB_2$  and the saturated one  $AB_3$ . Thus  $A$  would behave like a trivalent element, nitrogen.



In this way we see that when  $A$  acts as the centre round which the layer of electrons is arranged, it behaves like an element whose valency is equal to  $(8 - \text{number of electrons in the outer layer of the atom } A)$ .

There is, however, another way in which the atoms might combine, in this  $A$ , instead of receiving electrons from other atoms, might give up its electrons to help to form a layer round another atom. Take, for example, a two-electron atom  $B$ , by using one of its electrons it can attach itself to a seven-electron atom and still have one electron free. It can use this free electron to bind itself to another seven-electron atom and thus form the compound  $BF_2$ , where  $F$  represents an atom of such an element as fluorine. Thus in this type of compound the atom with its two electrons would behave like a divalent element. A three-electron atom would be able to bind three atoms of fluorine and so on. In this type of compound the atom under consideration is acting, so to speak, as a giver and not as a receiver of electrons. The valency of the atom when acting in this way is equal to the number of its electrons. The electron theory thus, as I pointed out long ago,<sup>9</sup> leads in a very natural manner to an explanation of valency and it suggests conclusions very similar to those advanced by Abegg and Bödländer,<sup>10</sup> who ascribed to each element two valencies according as it was combined with a more electronegative or more electropositive element. The sum of the two valencies always being eight. We have in some of the elements notable examples of two valencies; take nitrogen as an example, whose atoms contain five electrons in the outer layer. If this combines with hydrogen, three atoms of hydrogen will saturate it, as they will bring the number of electrons in the layer round the nitrogen up to eight, the limiting number, thus in the compound  $NH_3$ , the nitrogen behaves as a trivalent element. But suppose that instead of combining with a hydrogen atom it combines with a chlorine one, which we assume to have seven electrons in the outer layer. One of the electrons from the nitrogen atom might join the layer round the chlorine one, bringing the number of electrons in the latter up to eight, and leaving four in the nitrogen atom. These four electrons can link up with four hydrogen atoms which will bring the number of electrons in the layer round the nitrogen atom

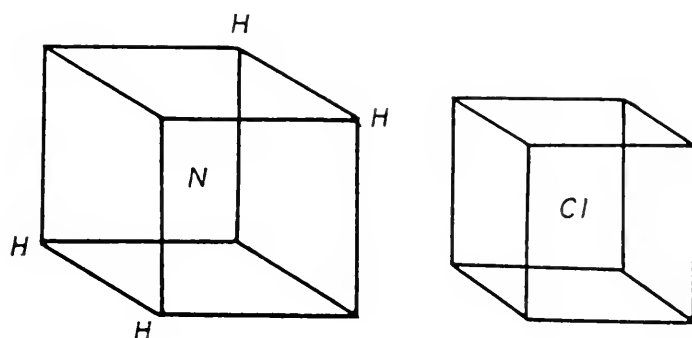
<sup>9</sup> *Phil. Mag.*, [6] 27, p. 757 (1914).

<sup>10</sup> *Zeit. Anorg. Chem.*, 20, p. 453 (1899); 30, p. 330 (1904).



up to eight, the limiting number. We thus get the compound  $\text{NH}_4\text{Cl}$ . The arrangement of the electrons being as represented in Fig. 11. As the chlorine nucleus has a positive charge of seven and is surrounded by a layer containing eight electrons, the atom  $\text{Cl}$  in this compound has a unit negative charge. Since there is a positive charge of five on the nitrogen nucleus and one of four on the four hydrogen atoms, there are nine positive charges on the system  $\text{NH}_4$ , which contains eight electrons:

FIG. 11.



there is thus a balance of one positive charge on the system represented by  $\text{NH}_4$ , so that  $\text{NH}_4\text{Cl}$  would, when electrolysed, give  $\text{NH}_4$  and  $\text{Cl}$  as ions.

Again each of the five electrons of the nitrogen atom might go off to complete the tale of eight electrons round each of five chlorine atoms forming the compound  $\text{NCl}_5$ ; though this substance does not seem to have been prepared, the corresponding compound  $\text{PCl}_5$  is well known. The oxygen atom containing six electrons might attach itself to six atoms of chlorine and so be apparently hexavalent, as sulphur is in the remarkable compounds  $\text{SF}_6$ , discovered by Moissan.

Carbon having four electrons in the outer layer has the same valency  $4 = 8 - 4$ , whether it is acting in either of the above-mentioned ways, hence the compounds  $\text{CH}_4$ ,  $\text{CCl}_4$ . The kind of union between atoms which we have been considering requires two electrons to effect the bond, hence since we cannot have more than eight electrons round a central atom, four is the maximum number of atoms which can be bound by a single atom. There are in fact very few exceptions to this rule, the most conspicuous are the chlorides of some of the elements which have very variable



valencies, such as  $\text{UrCl}_5$ ,  $\text{WCl}_5$ ,  $\text{MoCl}_5$ , which will be considered later.

Thus the considerations we have been discussing give a physical basis for the theory of valency in the extended form given by Abegg. The electron theory, however, is much more general than the laws of valency and points to the existence of compounds which are not in accordance with these laws. The electron theory states that any distribution of atoms and electrons in stable equilibrium is a possible compound and will be saturated provided that each electronegative atom is surrounded by a layer containing eight electrons.

Let us consider, as an example, carbon monoxide,  $\text{CO}$ ; this, according to valency laws, is an unsaturated compound, the gas is, however, remarkably inert and only liquefied with great difficulty, so that its physical properties give no support to the view that it is a highly unsaturated gas. In  $\text{CO}$  there are ten electrons to be arranged the same as in  $\text{N}_2$ , and we may therefore expect that a similar arrangement to that represented in Fig. 7 would furnish a stable and permanent molecule. As the positive charge on the carbon is not the same as that on the oxygen, the cell will not be so symmetrical as that of the nitrogen molecule. It is interesting to note that, as Langmuir has pointed out, some of the physical properties of  $\text{CO}$  are very similar to those of  $\text{N}_2$ . If this is the constitution of the molecule of  $\text{CO}$ , it explains why we do not get  $\text{CH}_2$  as a saturated substance, as the ordinary valency theory would lead us to expect. There are only six available electrons in  $\text{CH}_2$  and these are insufficient to produce a completely saturated layer. It is important to point out that we distinguish between the molecule of carbon monoxide and that of the carbonyl radicle  $\text{CO}$ .

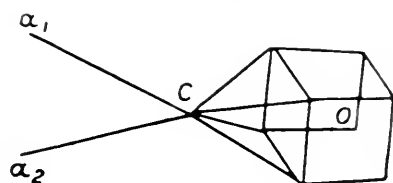
In the latter we suppose that two out of the four electrons of the carbon atom have gone to unite it with the oxygen and to make up the eight electrons required to form the layer round the oxygen atom, while the other two are free to join up with other electrons. Thus while the molecule of  $\text{CO}$  is represented by Fig. 7, that of the carbonyl radicle is represented by Fig. 12.

Another molecule which may have a somewhat similar constitution to that of  $\text{CO}$  is  $\text{NO}$ , Fig. 12a. The molecule contains eleven electrons, if we take eight of these to form the outer layer we are left with three, these by taking up positions between the



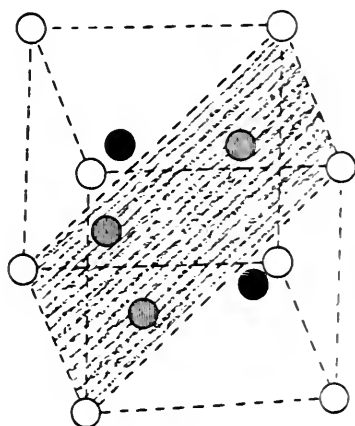
atoms of nitrogen and oxygen inside the outer layer may help to keep these atoms together. The molecule of nitrogen monoxide is not the only form in which the combination NO occurs; it can also exist as the radicle NO, and just as we suppose the carbonyl radicle to have a different configuration from that of the molecule CO, so we suppose that the radicle NO has a configuration in

FIG. 12.



which eight electrons form a cell round the oxygen, the nitrogen atom is surrounded by a layer of seven electrons made up of the three electrons left over after two have been supplied to the oxygen octet; the other four form part of the layer round the oxygen atom. The layer round the nitrogen requires another electron to saturate it and will thus act like a univalent atom. The

FIG. 12a.



three electrons left over from the five nitrogen electrons after two have been used to saturate the cell round the oxygen atom might be used to bind three hydrogen ions and thus it is possible that under certain circumstances this radicle might be trivalent.

Nitrogen monoxide is an example of the rare type of molecule where the number of electrons in the molecule is odd. Other examples of this type are  $\text{NO}_2$  and  $\text{ClO}_2$ . If we suppose that for stable substances an octet of electrons is formed round each



of the heavier atoms in the molecule, then if the number of electrons is odd, some of these octets must have an odd number of electrons, either one or three, in common. If we suppose the octets are cubes, they could not have three electrons in common, though they could have one, the two cubes having a corner in common. If, however, the electrons are arranged in twisted cubes instead of the ordinary cubes, two octets might have 1, 2, 3 or 4 electrons in common, since twisted cubes have triangular as well as square faces and thus we might have molecules containing an odd number of electrons with a less exiguous connection between the atoms than that furnished by a single corner common to two octets. The three-electron contact would account for the existence of a saturated compound with the formula  $\text{ClO}_2$ . We have here nineteen electrons and these might be accommodated in three octets if there was one double contact and one triple one.

Another problem in which the triple contact might come in, is the well-worn one of the benzene ring. In benzene  $\text{C}_6\text{H}_6$  we have thirty electrons which have to be arranged in octets round six carbon atoms. The simplest and most symmetrical way of doing this is to have the six cells in contact round a ring with a three-fold contact between each two. As two opposite triangular faces of the twisted cube are inclined to each other, this could be done without introducing much strain into the system. Models have been made by two of my students on this principle of a benzene ring and also of a naphthalene one. With this arrangement we have complete symmetry, and it is analogous to the Armstrong and Bayer or central theory of the benzene ring. The configuration corresponding to Kekules' conception of the constitution of the benzene ring would consist of three sets of pairs of cells, the cells in one pair having four-fold contact with each other, but only double contact with a cell in a neighbouring pair.

The three-contact view leads to results with regard to the constitution of addition compounds of benzene and the halogens which are in harmony with experience.

The process which we have just been describing by which two atoms  $A$ ,  $B$  are united into a molecule  $AB$ , of a compound may be regarded as consisting in one or more of the electrons in the outer layer of  $A$  becoming a member of the outer layer of  $B$ . This is equivalent to one of the electrons in the outer layer of  $B$



becoming a member of the outer layer of *A*. Thus each atom lends electrons to the other to enable it to fill up its outer layer; the atoms share their electrons for this purpose and the electrons which they have in common tend to hold the two atoms together. I think it is desirable to emphasize this aspect of the question, to regard the union of the two electrons as a sharing of their electrons rather than as the robbery of one atom of the electron belonging to another. I doubt if there is any very large change produced in gaseous compounds by chemical combination in the distance of an electron from the centre of the atom to which it originally belonged. I do not mean that the distance remains unaltered, but only that there is no such change in distance as would warrant our saying that the electron was bound to *B* before combination and was free afterwards. To tear electrons from an atom requires a much larger amount of work than to separate a molecule into uncharged atoms, and though there may be a redistribution of the electric charges on the molecule, there is nothing which can fairly be described as ionisation. Thus to take a specific example we regard the constitution of a molecule of HF as consisting of a unit positive charge H outside an outer layer of eight electrons surrounding the fluorine atom with its positive charge of seven units, and though we may legitimately describe the molecule as consisting of a positively charged hydrogen atom and a negatively charged fluorine one, it does not follow, if the molecule were dissociated by a rise in temperature, that the product of dissociation would be a positively charged hydrogen atom and a negatively charged fluorine one. It would take much less energy to detach the positive hydrogen atom plus an electron than the positively charged hydrogen atom alone, so that the probable result of the dissociation would be a neutral hydrogen atom and a neutral fluorine one. This would not necessarily be the case if the dissociation were effected by a high-speed positive ray with an energy corresponding to many thousand volts, for then the hydrogen atom could receive energy far more than sufficient to detach it from the negative electron. The result to which we have been led that dissociation would yield neutral atoms is in accordance with experience, for we do not find that chemical changes in gases produced by a rise in temperature are accompanied by a rise in electrical conductivity unless the gases are in contact with hot metals, and in this case the increase in conductivity may be explained by ther-

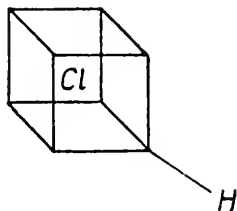


mionic effects. The absence of electrical conductivity in several cases of chemical action at moderate temperatures was investigated by Bloch,<sup>11</sup> who showed that the dissociation of arseniuretted hydrogen which takes place at low temperatures is not accompanied by any increase in the electrical conductivity. He also showed that many chemical actions which go on at low temperatures such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapours, have little or no effect on the conductivity.

#### POLAR MOLECULES.

Though in the gaseous molecule we have not ionisation in the sense that the atoms of the molecules are free to move in opposite

FIG. 13.



directions under the action of an external electric force, yet the disposition of the electric charges may be such that the molecules would tend to set in a definite direction under the action of such an electric force. The centre of the positive charges does not always coincide with that of the negative ones, so the molecule may have a definite electric moment. It is only in some type of molecules that this electric moment has a finite value. Thus in the symmetrical molecule formed by the union of two atoms of the same kind the centres of the positive and negative electric charges coincide and the molecule has no electrical moment. Whereas in a molecule like HCl, where the positive charge is outside the octet as in Fig. 13, the molecule has evidently a finite electric moment.

In other compounds such as  $\text{CO}_2$ , of which the arrangement is that in Fig. 14, there is complete symmetry. Thus, as I pointed out some years ago,<sup>12</sup> molecules may be divided into two types: (a) Polar, those having a finite electric moment; (b) Non-polar, those for which the electrical moment vanishes.

<sup>11</sup> *Ann. de Chimie et de Physique*, 22, pp. 370, 441; 23, p. 28.

<sup>12</sup> *Phil. Mag.*, 27, p. 757 (1914).

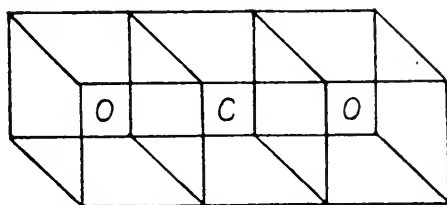


These two types will have very different properties. If the molecule has a finite electrical moment, it will give rise to an electric field whose intensity will vary inversely as the cube of the distance, while if the electric moment vanishes the force due to the molecule will vary inversely as some higher power of the distance and will thus die away much more rapidly than the forces due to a polar molecule; the latter will have a more extensive stray field and will attract and be attracted by a much larger number of other molecules.

#### PHYSICAL TEST FOR POLAR MOLECULES.

We shall first describe a test based on physical principles by which we can separate the polar from the non-polar molecule and

FIG. 14.



then see whether the molecules so separated show marked difference in their chemical properties.

The physical method for determining whether the molecule has a finite moment or not is the determination of the specific inductive capacity of the substances formed by the molecules, and if possible when the substance is in the gaseous state. The molecule with a finite moment will tend to set in a definite direction under the electric field, and this setting will contribute to the specific inductive capacity of the gas, hence such molecules will tend to give an abnormally high value to the specific inductive capacity. Again, since this setting of the molecule involves the rotation of the molecule as a whole, these will move so sluggishly that they will not be affected by vibrations as rapidly as those of light waves in the visible spectrum.

Hence these molecules will not affect the refractive index in the visible spectrum while they will affect the specific inductive capacity. We should expect, therefore, that the substances formed by such molecules would depart widely from Maxwell's law that



the square of the refractive index is equal to the specific inductive capacity. Again, since the setting of the molecules under the electric field will be hampered by the collisions with other molecules and as these collisions are more numerous and vigorous at high temperatures than at low, the specific inductive capacities of these substances will be affected by temperature and will diminish as the temperature increases. Bädeler<sup>13</sup> has determined the specific inductive capacities of many gases at varying temperatures, and it appears from his results that some of these gases, such, for example, as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{OH}$ , exhibit all these characteristics, they have specific inductive capacities which are much greater than the square of the refractive index and which diminish as the temperature increases.

Taking this as the criterion, we can find whether the molecules have or have not finite electrical moments and in the following tables, derived from measurements made by Bädeler and other observers, of the specific inductive capacity of gases, various compounds are placed in one or other of two classes.

TABLE I.

*Compounds which have a finite electrical moment.*

$\text{H}_2\text{O}$	$\text{CH}_3\text{OH}$
$\text{NH}_3$	$\text{C}_2\text{H}_5\text{OH}$
$\text{SO}_2$	$\text{CH}_3\text{Cl}$
$\text{HCl}$	$\text{CHCl}_3$ (slight)

TABLE II.

*Compounds which have not a finite electrical moment.*

$\text{H}_2$	$\text{CO}_2$
$\text{O}_2$	$\text{CS}_2$
$\text{N}_2$	$\text{CCl}_4$
$\text{He}$	$\text{C}_6\text{H}_6$
$\text{Cl}_2$	$\text{CH}_4$
$\text{CO}$	$\text{N}_2\text{O}$

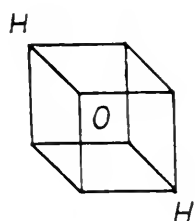
This list shows that the physical test we have applied separates the substances into two types which have great differences in their chemical properties. In the first type we have substances like water and alcohol which are good ionisers of salts or acids dissolved in them.

<sup>13</sup> *Zeit. für Physik Chem.*, **36**, p. 305.



The substances in the first table are also those which, like water, ammonia, and alcohol, are conspicuous in forming complex compounds with other salts, such as the hydrates, alcoholates, ammoniates. Another property which differentiates the substances in Table I from those in Table II is that of giving electrification by bubbling. When air or other gases bubble through some liquids, *e.g.*, water, alcohol, acetone, the gas when it emerges is found to be ionised, *i.e.*, mixed with positive and negative ions. Little, if any, electrification is found when a gas bubbles through a liquid like paraffin oil or benzene. This is shown very clearly

FIG. 15.



by the experiments of Bloch.<sup>14</sup> Liquids of the first type show electrification by bubbling, those of the second do not.

Molecules which contain the hydroxyl radicle OH, such as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , are usually polar; other organic radicles, such as  $\text{COOH}$ ,  $\text{CO}$ ,  $\text{CN}$ ,  $\text{NO}_2$ , also make the molecules of which they form a part polar. As the attraction of polar molecules extends over a much wider field than that of non-polar ones, we can understand why, though the hydrogen in saturated non-polar molecules such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  is not oxydised by weak solutions of sulphuric acid or bichromate of potash, the hydrogen in polar molecules such as  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$  (formaldehyde),  $\text{CHOOH}$ , is oxydised under the same conditions.

The fact that the polar molecule must be unsymmetrical gives us some information about the configuration of the electrons. One of the most interesting cases is that of water, which is conspicuous above all molecules for the possession of an electrical moment. Our first impression is that the structure of the water molecule should be that represented by Fig. 15, where the two hydrogen atoms are symmetrically placed with respect to the centre of the oxygen atom and the electrons are symmetrically distributed round the line joining the hydrogen atoms. This, how-

<sup>14</sup> *Ann. de Chimie et de Physique*, 23, p. 28 (1911).

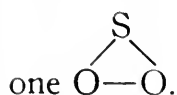


ever, cannot be right, for it would correspond to a molecule having no electrical moment. If the octet of electrons round the oxygen atom were situated at the corners of a cube, then there could be no question that a symmetrical arrangement of the hydrogen atoms with these atoms, respectively, attached to two electrons at the opposite ends of a diameter would be the position of equilibrium and this would correspond to a system having no electrical moment. If, however, the electrons were arranged at the corners of a twisted cube, no two electrons would be at opposite extremities of a diameter. Thus, if the positive atoms were attached to two electrons the system would be unsymmetrical and would have an electrical moment. Thus the electrical and chemical properties support the view that the electrons in the octet are at the corners of a twisted cube. The symmetrical position for the hydrogen atoms would, with the twisted cube, be when the positive hydrogen atoms are on the axis through the centre at right angles to the square faces. On this axis the positive atoms cannot be at a distance from the nearest electron less than half the diagonal of a square face. This distance is greater than would be necessary if the hydrogen atoms were placed close to the corners of the octet. This increase of distance would correspond to an increase of potential energy which might make the arrangement unstable. It would appear from these considerations that there may be more than one form of water. Thus the two hydrogens might be joined (*a*) to two electrons on the same square face or (*b*) one of the hydrogens might be joined to an electron on one square face and the other hydrogen to an electron on the other. Similar considerations would apply to the hydroxides of the alkali metals, but we should hardly expect the want of symmetry in these to be as pronounced as in hydrogen for the reason that the radius of say an atom of sodium is greater than that of one of hydrogen, so that these atoms might be able to get into the symmetrical positions without their distance from the nearest electron being increased much beyond that between the atom and electron in the uncombined atom. The effect of increased size may be illustrated by comparing water with methyl ether, which may be regarded as water in which the hydrogen atoms are replaced by the larger  $\text{CH}_3$  group. The specific inductive capacity of methyl ether and its dissociating power are very much smaller than those of water.

As another instance of the aid which considerations like these



may give in determining the structure of the molecule, we may take the case of  $\text{SO}_2$ . The determination of its specific inductive capacity shows that it has a finite electrical moment. It is therefore more likely to be represented by one of the unsymmetrical formulas  $\text{S}=\text{O}-\text{O}$ ,  $\text{O}=\text{S}-\text{O}$ , than by the more symmetrical



A molecule of a gas with a large electrostatic moment may itself promote combination between two gases, neither of which has molecules with a finite moment. Let us consider the effect of a molecule of this kind on the molecules of a gas near it. The intense electric field around this molecule will drag towards it the molecules around it; it will act as a nucleus round which the molecules of the other gas will condense. The nucleus will thus bring these molecules nearer together than they otherwise would be, and if like chlorine and hydrogen they can combine the presence of the nucleus, will assist combination. It seems possible that part of the action of water vapour in chemical combination may arise in this way, the interacting molecules crowding together so as to get into the strongest part of the electric field round the water molecules and thus getting into positions which are favourable for chemical combination.

In some cases the product of the chemical action will be active molecules with large moment. This will happen in the case of hydrogen and oxygen, or with hydrogen and chlorine, since the molecules of water and hydrochloric acid have a finite electrostatic moment. Here chemical combination promoted by the water vapour produces a fresh supply of active molecules and thus of nuclei which promote the combination. There will evidently be a tendency for mixtures of this type to become explosive. It is the intense electric field round a molecule with a finite electrostatic moment which causes the other molecules to condense round it. If, instead of a molecule with its electrostatic doublet, we had a charged ion, we should have a still more intense electric field and therefore might expect to get still greater condensation and more intense chemical action. The study of the conduction of electricity through gases gives us evidence of the existence of this condensation, as the ions in gases behave more like clusters than single molecules or atoms. It may be asked why is it that while



molecules possessing finite electric moments are able to promote so markedly chemical action, yet the speed of these actions is not noticeably greater in ionised than in non-ionised gases, though in the former the ions must produce intense electrical fields? The answer to the question is, that in any ordinary type of ionisation the number of charged ions is very small indeed compared with the number of molecules of a foreign constituent of the gas, even when the constituent is present as the merest traces. Take, for example, the case of water vapour, if the partial pressure of the water vapour were only the millionth of an atmosphere there would still be about  $2.8 \times 10^{13}$  molecules of water vapour per cubic centimetre. With such ionising agents as Röntgen rays, it is exceptionally strong ionisation when there are  $10^{10}$  ions per cubic centimetre, so that even with the amount of water vapour mentioned above, which it would be very difficult to avoid, even with the most careful drying, there would be about 2800 times as many molecules as there are ions in an intensely ionised gas. In cases where there are an exceptionally large number of ions present as, for example, in the negative glow in a discharge tube, all kinds of chemical actions seem to go on with great facility.

We shall see later on how these polar molecules are able to bring about dissociation of salts in liquids as well as promote chemical action.

It can be shown<sup>15</sup> that if  $M$  is the electrostatic moment of a molecule, *i.e.*, the product of one of the charges into the distance between the charges in an electric doublet which would produce the same electrostatic effect as the polar molecule; then  $K$ , the specific inductive capacity of the gas at the absolute temperature  $T$  and at a constant density corresponding to that at 760 mm. pressure and  $0^\circ$  C., is given by the equations

$$K = a + \frac{.88M^2 \times 10^{36}}{T} \quad (26)$$

where  $a$  is independent of the temperature. Hence measurement of  $K$  at two different temperatures would give us  $M$ .

Applying this formula to the results of Bädeker's experiments, I find that for water

$$M = 2.1 \times 10^{-18} \quad (27)$$

for ammonia

$$M = 1.5 \times 10^{-18} \quad (28)$$

---

<sup>15</sup> *Phil. Mag.*, 27, p. 763 (1914).

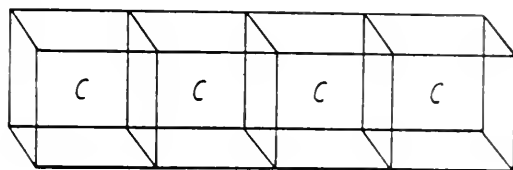


It is probable that determinations of  $K$ , and thereby of  $M$ , at different temperatures for different gases, would give us valuable information as to the lack of symmetry in the molecules of the gas.

#### ARRANGEMENT OF ELECTRONS IN OCTETS.

We have seen that when a shell of electrons surrounds a positive charge equal to the total charge on the electrons so that the system as a whole is electrically neutral, eight is the maximum number of electrons which can be in stable equilibrium on the shell. If some of the positive charge be taken from the inside of the shell and placed outside in symmetrical positions so as not to destroy the approach to sphericity of the shell of elec-

FIG. 16.



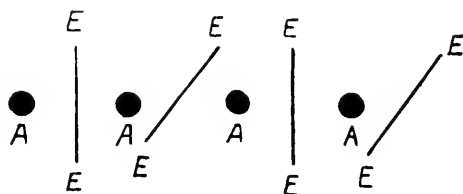
trons, we can prove that though this transformation will increase the radius of the shell, it will not in general increase the stability, and that eight will still be the maximum number of electrons which can, consistent with stability, be on the shell.

Thus confining our attention to systems such as those formed by collections of atoms where there is no excess of one kind of electricity over the other, eight will be the maximum number of electrons that can be included on a single spherical surface, while, if there are less than eight, the system will not be saturated. It follows from this that any system of electrons and atoms which is stable and saturated must consist of a number of cells of electrons, each cell containing eight electrons and having a charged atom inside. It does not follow that all configurations which can be built up in this way are possible, for though each cell might be stable if all the electrons and positive charges outside it were fixed, yet an aggregate of such cells need not be stable if all the electrons and atoms can move quite freely. Thus we cannot be sure that all distribution of electrons into octets represents a possible compound—as a matter of fact, we know that many do not. Thus to take a system of octets like that shown in Fig 16,



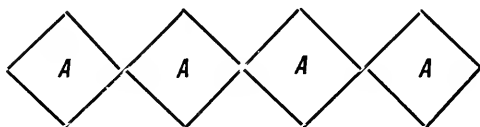
which represents a line of cubes placed face to face, each cube containing a positive charge equal to four. This is an electrically neutral system, and corresponds to a long line of carbon atoms. This system turns out on mathematical investigation to be unstable and therefore a long chain of carbon atoms cannot exist, but would break up into shorter chains, each containing 2, 3 or 4 atoms; this is in accord with chemical experience. On the other hand, long

FIG. 17.



chains of the radicle  $\text{CH}_2$  exist in many organic compounds. I have found that the analogous system consisting of a row of doubly charged positive atoms, each of which is at the centre of a tetrahedron of electrons as in Fig. 17, is stable. Take, as another example, a long row of cubes placed edge to edge as in Fig. 18, each cube containing a positive charge 6, this would form an electrically neutral system and would correspond to a long chain of oxygen atoms. The mathematical theory, however,

FIG. 18.



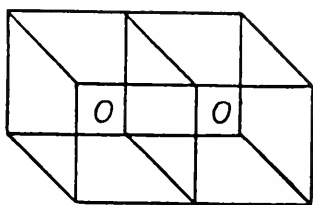
shows that this arrangement is unstable and this is confirmed by experience as compounds which contain even very short chains of oxygen atoms are highly explosive.

This division into octets may be regarded as a kind of entrance examination which every candidate for recognition as a formula representing the structure has to pass, and not as being necessarily either the right or even a possible formula. It is a necessary condition which every formula must fulfil, but it is not sufficient to ensure the stability of the compound. It was just the same on the old theory of valency; all kinds of compounds could be imagined which would satisfy the valency condition, but only a small fraction of these have been detected. In fact, chemistry is something more than freehand drawing.

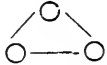


If we wish to find any arrangement of octets which can represent a molecule consisting of specified atoms, we have to solve the following problem. The number of electrons at our disposal is known because we know the atoms of which the molecule consists; we know the number of cells because there is to be one round each of the atoms which in a free state have four or more electrons in the outer layer. Thus we know the number of cells required and the number of electrons at our disposal; we have to see if it is possible to arrange the electrons in octets. If the octets were separate and did not go shares in any electrons, each cell would require eight electrons. Whenever we make an octet share an edge with another, we save two electrons; if it shares

FIG. 19.



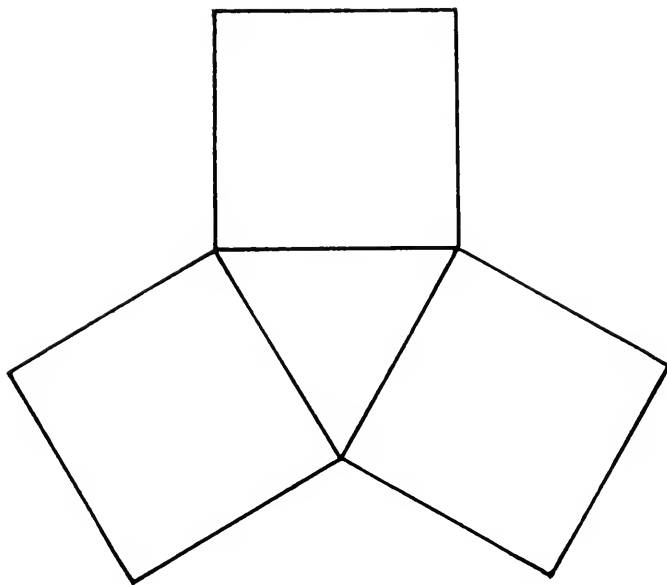
a triangular face, we save three; if it shares a square face, we save four. We have to try to find contacts between the octets of such a kind that the saving of electrons will equal the difference between eight times the number of cells required and the number of electrons at our disposal. Thus to take an example, suppose we want the arrangement for two oxygen atoms; here two cells are required and there are twelve electrons at our disposal; we have therefore to save four electrons by the contact between the two cells; to do this the octets must have a square face in common, so that the only possible arrangement is that represented in Fig. 19.

Suppose, however, we have three oxygen atoms to arrange in a molecule; hence we require three cells and we have eighteen electrons at our disposal; hence we have to save  $3 \times 8 - 18 = 6$  electrons by the contacts. We may do this in two ways: In one represented in Fig. 20, we have three line contacts, at each of which two electrons are saved. In the other, we have that represented in Fig. 21, where we have one line contact, saving two, and a face contact saving four. The first arrangement is represented by , the second by  $\text{O} = \text{O} - \text{O}$ ; which are



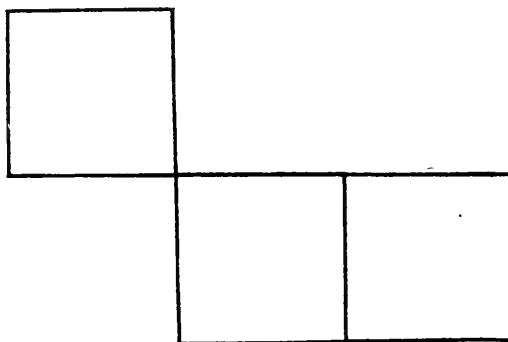
two possible formulas for ozone. If both are possible, there must be two kinds of ozone; the first of these being quite symmetrical would represent a molecule without a resultant electric

FIG. 20.



moment, the second we should expect to involve a finite moment. As we can detect the existence of electrostatic moments by experiment on specific inductive capacity, we may hope to find out

FIG. 21.



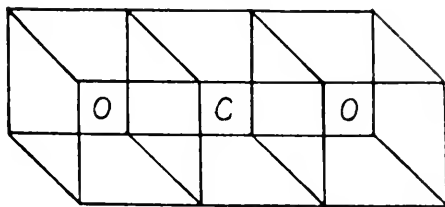
whether or not there are two kinds of ozone and, if there is only one, which is the formula which represents its constitution.

For  $\text{CO}_2$  we require three cells, and we have  $4 + 2 \times 6 = 16$  electrons. We have, therefore, to save  $3 \times 8 - 16 = 8$  electrons by the contacts; if the atoms are in a line there are only two of these, hence we have to save four at each contact, so that the



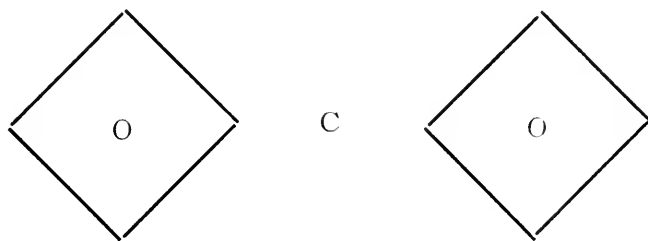
configuration will be that represented in Fig. 22. This configuration can also be regarded as a quadruply charged carbon atom placed midway between two oxygen atoms surrounded by octets of electrons, each of these systems carrying a charge  $-2$ , the molecule being represented by  $\overset{-2}{\text{O}}=\overset{4}{\text{C}}=\overset{-2}{\text{O}}$ . We may point out that we might have another configuration for the same distribution of electric charges, *viz.*, that represented by Fig. 23; here the

FIG. 22.



oxygen atoms carry the same charge as before, but they present an edge of the octet to the carbon atom instead of the full face. In this case we see that the layer of electrons nearest the carbon atom only contains four electrons, in that represented in Fig. 22 it contains eight. Thus this layer is saturated with the arrangement of Fig. 22, but not with that of Fig. 23. Thus if the electrons in  $\text{CO}_2$  were arranged as in Fig. 23, the molecule

FIG. 23.



would not be saturated; it could accommodate, for example, two molecules of water if these were arranged so that the water octet presented an edge to the carbon. While if they were arranged so that each of the water octets presented a point to the carbon atom instead of an edge, it could accommodate four molecules of water. If the oxygen atom also turned a corner to the carbon atom instead of an edge, there would be accommodation for six molecules of water. We thus see that where there are contacts such as those in Fig. 22, which are represented by double bonds



between the atoms, we can, by altering the orientation of the cells, make room for other neutral molecules or radicles. The whole number of system nearest to the central atom must not, however, exceed eight.

#### DISPOSITION OF THE ELECTRONS IN TYPICAL COMPOUNDS.

*Chlorides.*—Monochlorides, type  $\text{HCl}$ . We have here a positive charge outside the octet. The compound has a finite electrostatic moment. The region around the hydrogen atom is comparatively free from electrons, thus molecules of water could be held in stable equilibrium round the hydrogen ion, so that substances with this composition should be hygroscopic.

Bichlorides, type  $\text{CaCl}_2$ . A double positive charge between two octets; the molecule is non-polar. If each of the octets presents a face to the calcium atom, there will be eight electrons on a sphere round this atom; with this configuration there is no room for other molecules. If the chlorine octets swing round so as to present an edge instead of a face to the calcium atom, there will only be four electrons on the layer next to this atom. Thus there would be room for two water molecules if the water octets came edge foremost, or for four if they came point foremost. While if the chlorine octets were also point foremost to the calcium atom, there would be room for six molecules of water. We should expect these chlorides to be very hygroscopic.

An interesting fact about the halides is that we find chlorides such as tungsten hexachloride,  $\text{WCl}_6$ , and molybdenum pentachloride,  $\text{MoCl}_5$ , sulphur hexafluoride,  $\text{SF}_6$ , in which there are more than four atoms of chlorine or fluorine combined with one atom of another element. Now if each octet is to present an edge to the central atom, it will furnish two electrons to the layer round the central atom and as the number of electrons in this layer cannot exceed eight, it follows that there cannot be more than four atoms of one kind combined with one of another, a rule to which there are a few exceptions, such as these we are considering. We may explain the existence of these in two ways—one is to suppose that only four of the chlorine atoms are in the inner zone, that the other two are in the outer zone. In this case two chlorine octets carrying a negative charge would be easily detached, so that the compound should be a good electro-

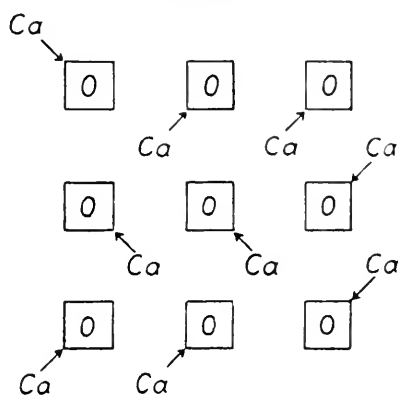


lyte. The other supposition is that all the chlorine octets are in the inner zone, but only two of them present an edge to the central atom, the other four only presenting a corner. The difference between the two is roughly that on the first supposition, two chlorine octets are loosely and four firmly held, while on the second two are firmly and four loosely held.

*Oxides.*—The points previously raised in connection with water apply to the oxides of the univalent elements generally.

Oxides of divalent elements of the type  $\text{CaO}$ . Here we have

FIG. 24.



the core of the calcium atom outside the oxygen octet. If this octet presents an edge towards the calcium atom, there will be room for three more octets, each presenting an edge, so that we can easily understand why this substance dissolves easily in water. It is not necessary that the octets which go to complete the tale round the calcium atom should be those of water molecules, they may be the octets of other  $\text{CaO}$  molecules. The fact that the octet of one molecule of  $\text{CaO}$  can also find its way into the inner zone surrounding other  $\text{Ca}$  atoms, will have a great effect in binding the different molecules together and thereby account for the very high melting points of the oxides. The arrangement in two dimensions when molecules of  $\text{CaO}$  mutually saturate each other is shown in Fig. 24. The arrow between  $\text{Ca}$  and  $\text{O}$  indicates that two electrons have gone from this particular calcium atom to complete the octet round the oxygen atom. The octets are supposed to present their edges to the calcium atom.

Sesquioxides, type  $\text{B}_2\text{O}_3$ . The most symmetrical arrangement for oxides of this type would seem to be one where the three oxygen octets have their centres at the corners of an equivalent



triangle, while the cores of the two boron atoms are symmetrically placed on an axis at right angles to this triangle and passing through its centre.

*Carbonates.*— $M_2CO_3$ . We have here three oxygen octets surrounding a central carbon atom. If the inner zone round this atom is to be saturated with electrons, one of the octets must turn a face, while the other two octets present edges, towards the carbon atom. If the octet turning its face to the carbon twists round and turns an edge, there will be room for another octet in the inner zone; thus the molecule can take up water or bind itself to other molecules of the carbonate. There would seem to be the possibility of two isomers, in one both the metal atoms are attached to the octets which present edges to the carbon; in the other, one metal atom is attached to the octet presenting a face and the other to one of those presenting an edge.

*Nitrates.*— $MNO_3$ . The arrangement is the same as for the carbonates, except that the central atom is nitrogen, with a positive charge of five and not carbon with a charge of four, and there is only one metal atom instead of two to put outside the octets. There is the possibility of two isomers as before.

*Sulphates.*— $M_2SO_4$ . Here we have four oxygen octets surrounding a central sulphur atom. These must have edges and not faces turned towards this atom. As all the four octets are turned the same way and are similar there will be no isomers.

*Perchlorates.*— $MCIO_4$ . The same as the preceding, except that the central atom is chlorine and not sulphur, and there is only one metal atom to place outside the octets.

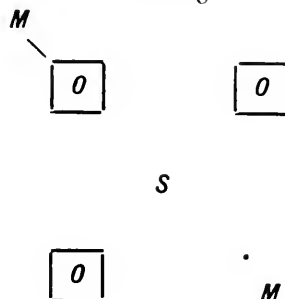
*Sulphites.*— $M_2SO_3$ . These from our point of view differ from the carbonates and nitrates because after providing for the electrons to furnish the three oxygen octets, there are still two electrons to provide for. The most symmetrical way would be to arrange them as in Fig. 25, *i.e.*, with one of the M atoms connected directly up with the sulphur and not indirectly through an oxygen octet. This would put the metal atom in the inner zone, from which we should not expect it to be detached in electrolysis; thus if M were hydrogen, this arrangement would correspond to a monobasic acid.  $H_2SO_3$  is, however, dibasic and therefore has probably both the H atoms connected directly with the oxygen and not with the sulphur. In this case we see that there are two electrons which have no direct connection with any



but the sulphur atom, and which would be available for attaching to the  $M_2SO_3$  molecule the positive part of any polar molecule or to complete the octet of an oxygen atom and thus form the sulphate.

*Chlorates.*— $MClO_3$ . Here we have the same number of electrons as in the sulphites, but the fact that the chlorates very readily give up oxygen while the sulphites take it up, suggests a

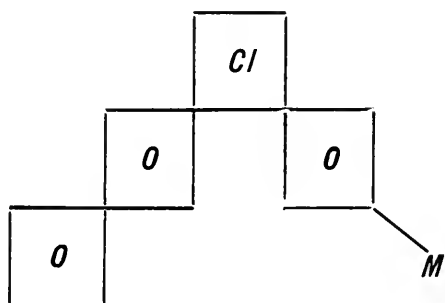
FIG. 25.



different grouping of the electrons. The arrangement given in Fig. 26, where one of the oxygen atoms is bound to another oxygen atom and not directly to the chlorine, would represent a molecule which would readily part with oxygen.

This arrangement of two oxygen octets with an edge in common is one that occurs in connection with the molecules of

FIG. 26.



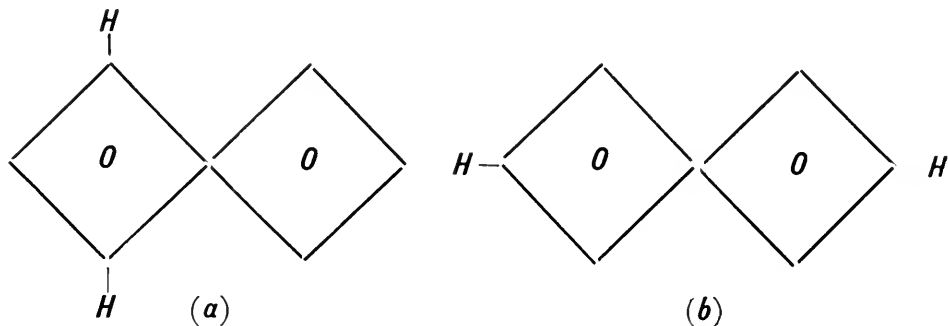
exceptionally intense oxidising agents, and we have already met with it when considering the form of the molecule of ozone. In hydrogen peroxide  $H_2O_2$  there are two possible forms, one represented by Fig. 27: (a) In which both hydrogen atoms are attached to the same oxygen octet, and the other (b) when one hydrogen atom is attached to one oxygen octet and the other to the other. In both cases we have two oxygen octets connected together by an edge. The first one would possess a finite electrical



moment, the second one would not, so that the forms could be distinguished by measuring the specific capacity of  $\text{H}_2\text{O}_2$  in the gaseous state.

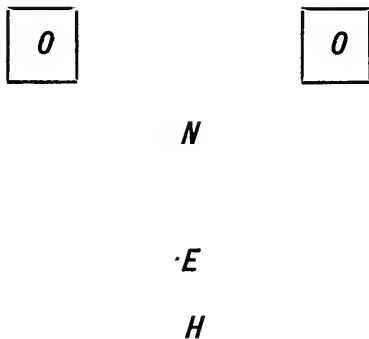
*Nitrites.*— $\text{HNO}_2$ . The nitrites resemble the sulphites in having two electrons which are not in direct connection with any

FIG. 27.



but the central atom. There are two oxygen octets and two electrons  $E$ , as in Fig. 28. If the hydrogen ion took up the position (H), it would be bound by these electrons, the hydrogen would be in the first zone and the substance would not be an acid. If

FIG. 28.



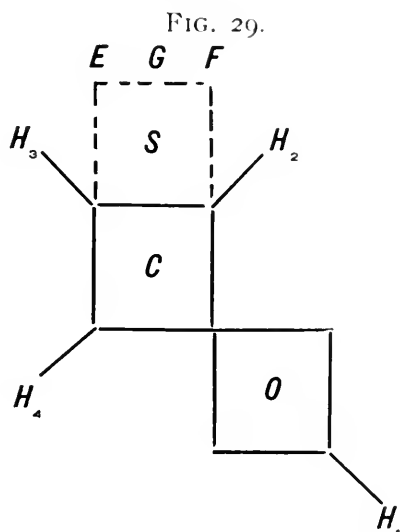
the hydrogen is attached to one of the oxygen octets, the substance will be an acid, and the two electrons will be free to complete the octet round a neutral atom of oxygen, link it up with the nitrogen, and convert the nitrite into a nitrate.

#### CONNECTION BETWEEN CHEMICAL CONSTITUTION AND CHEMICAL PROPERTIES.

If we know the distribution of the electrons and positive charges in a molecule, the behaviour of the molecule under specified physical conditions can be calculated from the forces



exerted on each other by the electric charges. The exact calculation in most cases would be a process of considerable length, but we can get without an appreciable amount of mathematics a general idea of the nature of the change in properties likely to be produced by changes in the composition of the molecule. The clearest way of illustrating the point in question is to take an example. Methyl alcohol  $\text{CH}_3\text{OH}$  is a substance without any tinge of acid properties; in fact, it is basic, if anything. When,

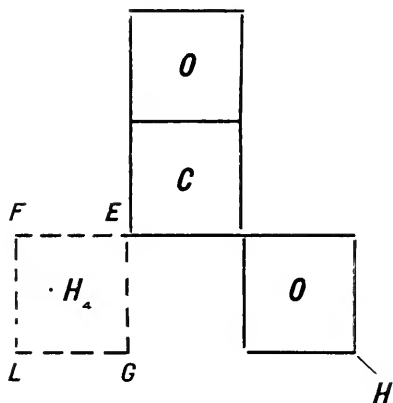


however, two of the hydrogen atoms are replaced by an oxygen one we get formic acid, a substance with pronounced acid properties. We know the general character of the distribution of electrons in the two cases, can we see why the difference in the distribution should make the difference between an acid and a feeble base? We shall suppose that the acid character of a substance containing the hydroxyl radicle  $\text{OH}$  depends on the ease with which the hydrogen ion  $\text{H}$  can be detached from the oxygen. We have therefore to see what is the difference between the force on the hydrogen ion in  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O.OH}$ . The arrangement of the electrons in methyl alcohol is represented in a general way by the continuous lines in Fig. 29, where for the sake of avoiding confusion in the drawing, the tetrahedral arrangement of the  $\text{H}_3$ ,  $\text{OH}$  atoms round the central carbon atom has been replaced by an arrangement in one plane. We have the octet round the carbon atom; the size of this does not vary much from one compound to another. We may thus regard this octet as occupying much the same position



in the formic acid as in the methyl alcohol. Consider the difference when we replace two of the hydrogens  $H_2, H_3$  by an atom of oxygen. We take away the positive charges  $H_2H_3$ , and replace them by a positive charge 6 at the centre  $S$  of the oxygen octet, and four negative electrons at the corners  $E, F$  of the face of this octet. Thus the difference between the forces on the atom  $H_1$  in the hydroxyl radicle in the methyl alcohol and formic acid is the difference between the force exerted by the positive charge 6 at  $S$ , by the four electrons on the face  $EF$  of the octet, and

FIG. 30.



that exerted by the two positive charges  $H_2H_3$ , which can be represented approximately by a positive charge 2 at  $S$ . Subtracting this from the charge 6 due to the oxygen, we see that the change due to substituting the oxygen for the two hydrogens can, as far as the forces are concerned, be represented by a plus charge 4 at  $S$ , and a charge on the whole amounting to  $-4$  carried by four electrons at the corners of the square face of the octet. If we replace these by a charge  $-4$  at  $G$ , the centre of the square face, then the force on  $H_1$  in the formic acid molecule will equal the force on  $H_1$  in the molecule of methyl alcohol plus the force due to the doublet with a positive charge 4 at  $S$  and a negative one  $-4$  at  $G$ . The effect of the doublet is, as will be seen from the figure, to repel  $H_1$  away from  $O$ . It will thus tend to detach  $H_1$  from the molecule, *i.e.*, to make the molecule act like an acid.

As a further example let us consider whether replacing a hydrogen atom in such a compound as formic acid by a chlorine one would increase or diminish the acid properties of the molecule.

Suppose that Fig. 30 represents the distribution of the



electrons in a molecule of formic acid. If the hydrogen  $H_1$  were replaced by chlorine, the change as far as the electrical forces are concerned will be that the charge  $+1$  at  $H_1$  will be replaced by a charge  $+7$  carried by the chlorine atom, and that six other electrons will be introduced which, with the two along the edge  $E$ , will make up the octet round the chlorine atom. To calculate the effect of these six electrons, we take the four along the edges  $F$  and  $G$ ; these are at the corners of a rectangle whose centre is at  $S$ , the centre of the chlorine atom. If these electrons act as if they were concentrated at the centre of figure  $S$ , they will have the effect of reducing the positive charge at the centre of the chlorine atom from 7 to 3. Now take the two electrons at the edge  $L$ ; these with two of the three charges at the centre of the chlorine atom will form an electrical doublet whose moment is  $2e \times LS$  with its positive part turned towards the centre of the molecule, the remaining positive charge at  $S$  will represent the positive charge on the hydrogen atom before it was replaced by chlorine. Thus the difference in the forces due to the replacement of hydrogen by chlorine is represented by the electrical doublet  $2e.LS$ , and this as we see from the figure will tend to drive off the hydrogen in the hydroxyl radicle—thus the substitution of chlorine for hydrogen tends to increase the acidity of the molecule. This is very strikingly shown by monochlor, dichlor and trichlor acetic acids, which are much stronger acids than acetic acid itself.

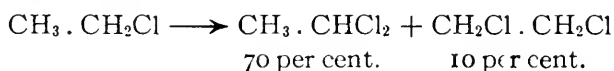
It follows from the investigation we have just given that if in a hydrocarbon such as  $CH_4$  we substitute for one of the hydrogen atoms  $E$ , the atom of an electronegative element such as chlorine, the change in the electric forces can be represented by the introduction of an electrostatic doublet at  $E$  with its axis along  $CE$  and the positive part of the doublet turned towards  $C$ . The molecule of  $CH_4$  before the substitution of the chlorine atom was non-polar, *i.e.*, the molecule had no electrostatic moment, the substitution of the chlorine for the hydrogen introduces a finite electrostatic moment and thus makes the molecule polar.

The positive part of the doublet at  $E$  is turned towards  $C$ , hence the force it produces at  $F$ ,  $G$ ,  $H$ , the other corners of the tetrahedron whose centre is at the carbon atom, will tend to attract negatively and repel positively charged atoms. Hence if a molecule of  $CH_3Cl$  were placed under such conditions that there

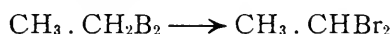


were positively and negatively charged atoms in its neighbourhood, the concentration of the negative atoms round *F*, *G*, *H* would be greater than it would be for the molecule  $\text{CH}_4$  before the hydrogen at *E* had been replaced by the electronegative chlorine. Thus the substitution of the atom of an electronegative element for one of the hydrogen atoms round the carbon will tend to promote the substitution of electronegative atoms for the remaining hydrogen atoms. If two of the hydrogen atoms are replaced by an atom of oxygen, this will for the same reason promote the substitution of electronegative atoms for the other two hydrogen atoms. We have illustrations of this effect in the following examples for which I am indebted to Mr. W. H. Mills.

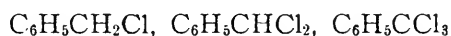
Ethyl chloride + chlorine (1 molecule) in the liquid state under the influence of ultra-violet light,



Ethyl bromide heated with bromine in sealed tube,



Chlorine on boiling toluene ( $\text{C}_6\text{H}_5 \cdot \text{CH}_3$ ) in sunlight gives successively



We see from these examples that there is a tendency for a new hydrogen atom to go into that part of the molecule which is already halogenated.

In the presence of catalysts such as ferric bromide, the halogen atoms in the higher members of the series go to the carbon atom adjacent to the one already brominated.

Another illustration of this effect is the well-known fact that when an organic compound is oxidised the carbon atom attacked is the one which already is attached to oxygen.

I pass on now to consider a problem which I can best explain by stating a particular case. Why is it that in a compound such as methyl alcohol  $\text{H}_3\text{C} \cdot \text{OH}$  the only atom of hydrogen which is replaceable by a monovalent metal is the one in the hydroxyl radicle. Or to take another aspect of the same problem, why can the hydrogens in marsh gas not be replaced by the monovalent positive elements, while they can be replaced by the monovalent negative ones like Cl, Br, I? Let us consider what are the conditions for the existence of  $\text{CH}_4$ . We have an octet of electrons



round the carbon atoms. The carbon atom which only carries a charge of four units could not by itself keep eight electrons in stable equilibrium. It is enabled to do this by the stabilising effect of the positive charges which are on the hydrogen atoms. This stabilising effect will depend on the distance of the positive charge on the hydrogen from the nearest electron in the octet, a distance which we should expect to be not greatly different from the radius of the hydrogen atom. Consider now the effect of replacing the hydrogen atom by one of an alkali metal; the radius of the atom of the alkali metal is very considerably greater than that of the hydrogen atom. The control over the electron in the metal is much less than that on the electron in the hydrogen atom. This is shown by the fact that the ionising potential for the hydrogen atom is much greater than that for the metal one, thus we should expect the stabilising effect of the positive part of the metal atom to be very considerably less than that of the hydrogen atom. Thus while the stabilising effect of the hydrogen atom may be great enough to make the octet of electrons round the carbon atom stable, that of the metal atom may not be able to do so, in which case the metallic compound could not exist.

In this view the atoms of the monovalent metals are not efficient stabilisers of an octet of electrons, and we should expect that in the compounds they form the octet should be of a kind that requires little help from the positive charge on the metal atom to make it stable.

Let us consider a few types of the salts formed by these monovalent metals. Let us begin with the chlorides, here we have an octet of electrons round the chlorine atom and the positive charge outside. Now experiments with positive rays show that a neutral chlorine atom, having seven electrons in the outer layer readily takes up a negative charge, *i.e.*, acquires another electron. Thus an octet of electrons round a chlorine atom is stable even without the assistance of an external positive charge, and thus a metal atom outside an octet round a chlorine atom will be a system where the octet is very stable. Hence we should expect that all these alkali metals would, as in fact they do, form chlorides readily. Now let us turn to the hydroxides. The neutral hydroxyl radicle has seven electrons arranged round the oxygen atom. Now again experiments with positive rays show that the hydroxyl radicle very often occurs with a negative charge and in



this state there must be an octet of electrons round the oxygen atom. Thus such an octet with the hydrogen atom outside is stable by itself even without assistance from the positive part of a metallic atom. Thus when it gets this assistance the octet will be very stable, so that we should expect, as in fact is the case, that the hydroxides of the alkali metals would be formed very readily.

Now let us turn to the oxides, here we have an octet round the oxygen atom and the positive part of two metallic atoms outside. As lines corresponding to negatively electrified oxygen atoms are to be seen on nearly every positive-ray photograph, a system of seven electrons round the oxygen atom must be a stable system. In the case of the metallic oxides we have two positive charges to make the system stable when another electron is added. We have seen from the case of hydroxyl that a single hydrogen atom is able to bring about this stability, so that as two metal atoms are available the metal atoms would have to be very inferior to the hydrogen one as stabilisers if the octet were not fairly stable.

Now let us consider why it is that, while we cannot replace by a metal one of the hydrogen atoms directly connected with the carbon atom in a hydrocarbon, we can replace the hydrogen in a hydroxyl group linked up to the carbon. Let us take methyl alcohol as an example, where we may suppose the electrons are arranged as in the diagram. We see that from its position the hydrogen in the hydroxyl group has little to do with the stability of the octet round the carbon atom; it is the stability of that round the oxygen atom with which it is concerned. Now an octet round an oxygen atom is a very different thing as far as stability is concerned from one round a carbon atom. We have seen that seven electrons can be in stable equilibrium round an oxygen atom without any help from systems outside and that a single positively charged hydrogen atom outside is sufficient to make the octet stable. If the hydrogen in the hydroxyl is replaced by a metallic atom, then to keep the octet round the oxygen atom stable we have not only the positive part of the atom of the metal, but also that of the carbon atom with its attached electrons and positive hydrogen atoms. Thus the conditions are much more favourable for the stability of this octet than they are for that round the carbon atom, and thus it may be possible to replace the hydrogen in the hydroxyl but not that in the rest of the atom.



The positive rays afford evidence that to make the octet of electrons round the carbon stable in a compound  $\text{CH}_3\text{X}$ , where X is a monovalent element, assistance is required from X. For if it were not, the system got by removing the positive part of X would be stable, but this system is just the radicle  $\text{CH}_3$  with a negative charge. Now the line corresponding to this radicle occurs frequently in positive rays, but always with a positive charge, while other radicles, such as OH, are found with negative as well as with positive charges. This is an indication that the stability of the octet round the carbon atom depends upon the presence of X. On the other hand, if the residue after taking away an atom of hydrogen from a hydrocarbon is stable even after receiving a negative charge we should expect that the hydrogen atom might be replaced by an atom of the metal, for the molecule is stable after the hydrogen has been removed and the octet does not depend on the positive charge for its stability. Now on many positive-ray photographs I have observed a line corresponding to a molecule with a negative charge, whose molecular weight is 25, when hydrocarbons were in the discharge tube. The molecular weight indicates that the molecule is  $\text{C}_2\text{H}$ , *i.e.*, acetylene minus an atom of hydrogen, if this is so the hydrogen in acetylene might be replaced by a metal: The compound  $\text{C}_2\text{Cu}$  which is of this type is well known.

Though we have seen the stability of the oxides indicates that the octet round the oxygen atom can be stabilised by the presence outside it of the positive parts of metallic atoms, there are indications that this octet is not so stable as those in the chlorides and hydroxides. The main evidence is that many oxides and sulphides when in the solid state are conductors of electricity, especially at high temperatures, and that, as the researches of Königsberger and Horton show, this conductivity is not electrolytic, but resembles that through metals. There are some chlorides which conduct in the solid state, but as far as I am aware their conductivity is always electrolytic. The conductivity of metals can, as we shall see, be explained as due to electrons which move freely about in certain directions through the solid. So that the non-electrolytic conductivity of these oxides and sulphides indicates that some electrons have got free, *i.e.*, that some of the octets round the oxygen and sulphur atoms have broken up. This breaking up increases very rapidly with the temperature. Another piece of



evidence to the same effect is the very intense thermionic emission by oxides such as those of calcium, strontium and barium, an emission which, as Horton has shown, is far more intense than that from the metals themselves at the same temperature. On our view this is due to the breaking up of the octets round the oxygen atoms. The smaller the charge on the neutral atom, the more will the stability of the octet round it depend on the positive charges outside. Thus as nitrogen has only a charge 5 while oxygen has one of 6, we should expect the octet round nitrogen in a metallic compound to be more easily broken up than that round oxygen in metallic oxides. It would be interesting to test from this point of view the properties of tripotassiumamide,  $\text{NK}^3$ .

RESIDUAL AFFINITY, MOLECULAR COMPOUNDS, WERNERS  
COÖRDINATION NUMBERS.

We have regarded the molecule of a chemical compound as made up of atoms some of which have lost electrons, while others have gained them, so that the former are positively, the latter negatively, electrified; the forces between the electrical charges on the atoms and electrons binding the atoms together in such a way as to form a stable system. The number of electrons which an atom can gain or lose depends upon the nature of the atom. The number it can lose is equal to the number of electrons in the outer layer, and varies from one to eight according as the element belongs to one or other of the Mendeleefian groups; the number it can receive is 8 minus the number in the outer layer.

If the transference of electrons has proceeded to its limit, *i.e.*, if every positively charged atom has received the maximum positive charge of electricity it can acquire and every negatively charged one its maximum charge of negative electricity, there must be simple relations between the number of different kinds of atoms in a neutral molecule. Thus, for example, if we have two kinds of atoms, *e.g.*, calcium and chlorine, since the neutral calcium atom has two electrons in its outer layer and the neutral chloride seven, the calcium atom can lose two electrons while the chlorine atom can only gain one. We see therefore that when the transference of electrons has gone as far as possible, each calcium atom will have given up its electrons to two chlorine atoms neither more or less and thus for each calcium atom positively charged



there must be two chlorine ones with negative charges, thus the composition of the molecule would be represented by the symbol  $\text{CaCl}_2$ . And we can show easily that when the transference of electrons has proceeded to the limit the proportion between the numbers of the various kinds of atoms in the molecule will be the same as that deduced from the ordinary principles of valency.

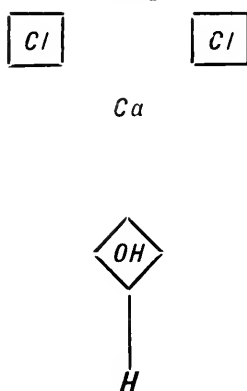
In such a molecule as  $\text{CaCl}_2$  the transference of electrons has reached its limit, and as far as this property is concerned the molecule may be regarded as "saturated." Unfortunately there has been a tendency to regard this "saturation" as applying to quite a different thing. Some chemists have supposed not merely that the calcium atom when it had charged two chlorine atoms had exhausted its power of charging up any more atoms negatively, which is true, but they implied, which is not true, that the doubly charged calcium atom cannot by its attraction hold more than two atoms in stable equilibrium. It is important to distinguish between the maximum positive charge the atom can acquire and the maximum number of negatively electrified systems which the maximum charge can hold in stable equilibrium in a single layer around it. The table given in the first chapter shows that when the attractive force between the positive charge and a negative one is represented by  $\frac{a}{r^2} - \frac{b}{r^n}$ , the number of negative charges which a positive charge can hold in stable equilibrium in a single layer is, when the positive charge does not exceed a limit determined by the value of  $n$ , greater than the number of units of positive charge on the central system. This is confirmed by the fact that the positive-ray method reveals the existence of negatively charged atoms, for example, the atoms of hydrogen, carbon, oxygen, chlorine are frequently found to be negatively charged, and a negatively charged atom must have more electrons than the number of units of positive charge. Thus, though a calcium atom could not itself charge negatively more than two chlorine atoms, yet if a third chlorine atom, negatively electrified by some external agent, were brought near the calcium atom, it would hold it in stable equilibrium and form the system  $\text{Ca} \text{ } ^{+2}\text{Cl} \text{ } ^{-}\text{Cl} \text{ } ^{-}\text{Cl} \text{ } ^{-}$ . This system would, however, be negatively charged and so could not be expected to remain free under normal conditions; it might, however, be found in electrolytes or charged gases. There may, however, be electrically neutral compounds in which the calcium



atom is surrounded by more than two systems. Let us suppose that instead of bringing up a negatively electrified chlorine atom to the  $\text{CaCl}_2$ , we bring up a molecule which possesses considerable electrical moment, *i.e.*, one in which the positive and negative parts are separated by a considerable distance, such, for example, as a molecule of water  $\text{H}(\text{OH})$ . The negative end of this would place itself closer to the calcium than the positive one and we should get a system such as that represented in Fig. 31.

This system as a whole is electrically neutral and so could exist

FIG. 31.



under normal conditions; it would be held together by forces of just the same type as those which hold the atoms together in  $\text{CaCl}_2$ , yet from the ordinary chemical point of view the latter is a valency compound while the former is not.

It must be noticed, however, that though the number of systems that can exist round the central atom may be greater than the positive charge on that atom, theory indicates that there is a sharp limit to this number, so that the possible compounds of this type would be determined by definite rules.

We can get some information about the number of atoms or molecules which can be grouped in stable equilibrium about a central system  $S$  by applying the condition for stability which we have already used when considering the stability of arrangements of electrons in the atom. Let us suppose that the atoms grouped around  $S$  are the centres of octets of electrons, the electrons in these octets which are nearest to  $S$  will furnish a layer of electrons round  $S$  and for stability the number of electrons in this layer must not exceed eight. The number of electrons an octet will supply to this layer will depend upon the orientation of the octet.



If  $O$  is the centre of the octet, then if  $SO$  passes through an electron, *i.e.*, if the octet presents a corner to  $S$ , it will supply one electron to this layer. If  $SO$  bisects at right angles the line joining two electrons on the octet, *i.e.*, if the octet presents an edge to  $S$ , two electrons will be supplied, while if  $SO$  is at right angles to a face of the octet, *i.e.*, if the octet presents a face to  $S$ , four electrons will be supplied. When all the octets present corners to  $S$  the maximum number around  $S$  will be eight. Considering the exiguous character of this connection between  $S$  and the octets, we should not expect this arrangement to have any very great stability. If each octet presents an edge to  $S$ , the maximum number of octets will be four, while if each presents a face to  $S$ , the maximum number will be two. Thus the number of systems which can be held in stable equilibrium in the first zone round  $S$ , which following Werner we shall call the coördination number of  $S$ , may vary from 2 to 8. Werner finds that an appreciable number of elements have a maximum coördination number four, a few have eight, the number for the majority is, however, six, which would correspond to four of the octets presenting a corner, and two an edge to  $S$ .

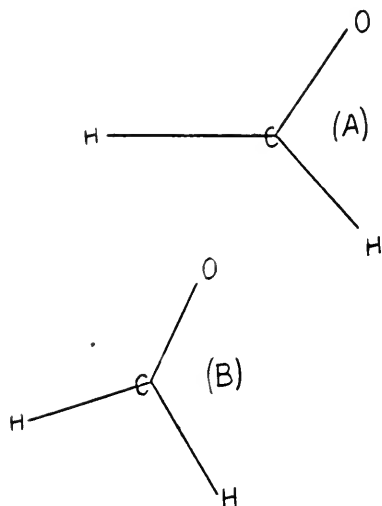
The coördination number is never less than the valency and is generally greater. The somewhat vague notion implied by the use of the term "Residual Affinity," which appears frequently in chemical literature, is an attempt to give expression to the facts implied by a difference between the valency and the coördination number. The consequences of this difference are of the first importance. Let us see, for example, how it would facilitate the aggregation of molecule. Let us take as an example formaldehyde  $\text{COH}_2$ , a substance which is saturated for valency purposes, but is not coördinately saturated. Thus if  $A$  (Fig. 32) represents a molecule of formaldehyde, then if the coördination number of carbon is four,  $A$  can hold another negatively electrified oxygen atom in its shell; this may form a part of another formaldehyde molecule  $B$ , and thus  $A$  and  $B$  may be held together in the way indicated in Fig. 32. As  $B$  is not coördinately satisfied, it may link up with the oxygen from a third molecule  $C$ ; in this way aggregates of the formaldehyde molecule would be formed readily.

We can apply to the union of molecules considerations quite analogous to those we applied to the combination of atoms. Thus, for example, we can picture two molecules of  $\text{Li Cl}$  joined together



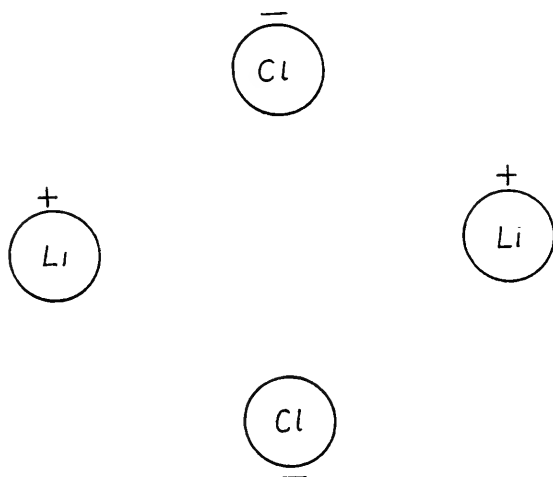
by an arrangement like Fig. 33, which is similar to that binding two atoms of lithium together, the electrons in the latter being replaced by negatively electrified atoms in the chloride. Indeed,

FIG. 32.



if the coördination number were always eight, the molecular compounds would run quite parallel with the atomic ones, *e.g.*, the atoms would be arranged in octets in the molecular compounds

FIG. 33.



just as the electrons are arranged in octets in the atomic ones. Since eight is the maximum number of electrons which can be arranged in one layer round a central atom, eight is the coördination number of an atom with respect to electrons; hence when the coördination number in molecular compounds is eight, we see



that the molecular compounds will run parallel to the atomic ones. Let us apply this result to a particular case. We saw that when the atoms of an element contain few electrons, so few that these are not sufficient in a diatomic molecule to make up the total of eight, the molecules have a great attraction for each other, so that the element under normal conditions is in the solid state, *e.g.*, Li, Be, Bo, C. When, however, there are sufficient electrons in the atom for the atoms in a diatomic molecule to make up, by sharing electrons, one or more octets, the molecules have but little attraction for each other, and the element is gaseous, *e.g.*, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, Ne. Considerations of exactly the same character will apply to the molecular compounds formed, for example, by the chlorides. A chloride like NaCl, which contains only one chlorine atom, is analogous to an atom containing only one electron; a chloride like BeCl<sub>2</sub>, which contains two chlorine atoms, to an atom containing two electrons and so on. The molecules formed by atoms which contain less than five electrons exert great attractions on each other and condense into the solid state, while those containing five or more electrons are much more volatile and for the elements in the first period are gaseous. The result we have just obtained shows that we may apply to the chlorides the same reasoning as we applied to the atoms. Hence we should expect those chlorides which contain only a small number of chlorine atoms, to be solids; while those containing more than a certain number of chlorine atoms should be much more volatile. The following table of the boiling points of the different chlorides and fluorides shows that this is the case to a very marked extent.

The number of halogen atoms corresponding to a volatile or non-volatile substance will depend upon the coördination number of the element with which the halogen atoms are combined. The smaller the coördination number of the element, the smaller the number of chlorine atoms required to make the chloride volatile. As the coördination number varies from element to element, the connection between volatility and the number of chlorine atoms cannot be expected to be as clear cut as that between the volatility of an element and the number of electrons in the atom, when the coördination number of an atom with respect to an electron is always eight. The non-volatility of some of the chlorides such as WCl<sub>5</sub>, WCl<sub>6</sub> is, I think, due to the chlorine atoms being in two layers, so that the number in the outer layer, which



*Compounds Containing One Halogen Atom.*

Name.	Formula.	Melting point.	Boiling point.
Sodium chloride	NaCl	776	
Silver chloride	AgCl	450	
Sodium fluoride	NaF	above 902	

*Compounds Containing Two Halogen Atoms.*

Calcium chloride	CaCl <sub>2</sub>	720	
Magnesium chloride	MgCl <sub>2</sub>	708	
Strontium fluoride	SrF <sub>2</sub>	above 902	
Calcium fluoride	CaF <sub>2</sub>	above 902	
Stannous chloride	SnCl <sub>2</sub>	250	620

*Compounds Containing Three Halogen Atoms.*

Antimony trichloride	SbCl <sub>3</sub>	73	223
Bismuth trichloride	BcCl <sub>3</sub>	230	430
Boron trichloride	BCl <sub>3</sub>	liquid	18

*Compounds Containing Four Halogen Atoms.*

Silicon tetrachloride	SiCl <sub>4</sub>	liquid	50
Stannic chloride	SnCl <sub>4</sub>	liquid	114
Titanium tetrachloride	TiCl <sub>4</sub>	liquid	135
Silicon tetrafluoride	SiF <sub>4</sub>	gas	

*Compounds Containing Five Halogen Atoms.*

Antimony pentachloride	SbCl <sub>5</sub>	gas	
Molybdenum pentachloride	MoCl <sub>5</sub>	194	268
Tungsten pentachloride	WCl <sub>5</sub>	248	278

*Compounds Containing Six Halogen Atoms.*

Sulphur hexafluoride	SF <sub>6</sub>	gas	
Tungsten hexachloride	WCl <sub>6</sub>	275	346

determines the volatility, is less than the number of chlorine atoms in the compound.

Another example of the analogy in physical properties for similar proportions between the number of electrons in the atom and the number of chlorine atoms in a chloride is afforded by the consideration of the electrical properties of the elements and of chemical compounds.

When there are less than four electrons in the outer layer of an atom of an element, the element is a metal and a good conductor of electricity, the conductivity arising from the movement



of the electrons; when there are more than four electrons in the outer layer the element is a bad conductor of electricity. The electrical conductivity of fused chlorides may be compared with that of the metals, the negatively electrified chlorine atoms taking the place of the electrons and making the conduction electrolytic. Chlorides containing a small number of chlorine atoms are good conductors when fused, while the higher chlorides like  $\text{SnCl}_4$ ,  $\text{CCl}_4$  insulate, although they are in the liquid state.

The thermionic properties of metals find, too, a parallel in those of the chlorides. A metal contains lattices of positively electrified atoms and electrons, the solid chlorides, lattices of the atoms of the metal and of negatively electrified chlorine atoms, and the work required to eject a chlorine atom from the salt would be of the same order as that required to eject an electron from the metal. Again, the proportion between the number of atoms and electrons in the metal would be the same as that between the number of metal atoms and of chlorine atoms in its chloride. Hence we should expect from thermodynamic considerations that at temperatures at which the thermionic emission of electrons from the metal is considerable, there should be an emission of negatively electrified chlorine atoms from the salt. Such an emission does in fact take place.<sup>16</sup> When salts are first heated considerable currents are carried by the chlorine atoms and no electrons can be detected. The effects produced by prolonged heating are very complicated, more so even than those occurring on the emission of electrons from hot metals. This is what we might expect, as the tearing away of the chlorine atoms would produce a more fundamental change in the surface than the emission of electrons from a metal. After prolonged heating electrons, as well as chlorine atoms, are given off, suggesting that the tearing away of the chlorine atoms has produced an excess of metal atoms at the surface.

When the coördination numbers of the metals occurring in double salts are not all equal, the arrangement of the electro-negative atoms round the atom of the metal will not be in octets, but one which provides a layer of negative atoms round each atom equal to the coördination number of that atom.

Before leaving the consideration of the coördination number we must raise the question whether a doubly charged atom like

---

<sup>16</sup> Richardson, "Emission of Electricity from Hot Bodies."



oxygen ought to count as two towards the coördination number as it does towards the valency. If we take the view before discussed, the oxygen atom for coördination purposes ought to count as one and not as two. On that view the limits to the coördination number depend on the octets round the central atom. An octet with a double charge, such as that associated with an oxygen ion, can be orientated so as not to bring more electrons into the layer next the central atom than an octet with a single charge like that associated with a chlorine ion, thus the oxygen need not count for more than the chlorine.

#### ELECTROLYTIC DISSOCIATION.

When the coördination number of the central atom is greater than its valency, the molecule can combine with polar molecules such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  to form new compounds in which the atoms in the original molecule are driven further apart, and are therefore able to rearrange themselves with the expenditure of much less energy than would have been necessary if these compounds had not been formed. Positively and negatively charged atoms may in this way be thrust so far apart and the connection between them made so slight that they move in opposite directions under the action of an electric field, and are thus resolved into ions.

This is well illustrated by the well-known example given by Werner of the ammoniates of platinic chloride. If the coördination number of platinum is six, then in  $\text{PtCl}_4$  there is room for two polar molecules in the first layer round the platinum atom without that layer becoming unstable. The chlorine atoms are in direct connection with a platinum atom and so cannot be detached easily from it. Thus the compound  $\text{PtCl}_4(\text{NH}_3)_2$  is not an electrolyte. If, however, more molecules of  $\text{NH}_3$  are added, since 6 is the maximum number of constituents which can be in one layer round the positive charge, the constituents in the inner layer must break up into two groups, one group forming a layer of six next the platinum, the remainder forming an outer layer at some distance from the inner one. The process is very closely analogous to that described in Chapter I when new layers of electrons were formed when the number of electrons in the atom exceeds the number which can be held in stable equilibrium in one layer by the central positive charge.

Thus if four molecules of ammonia are added to the platinic



chloride, there must be two constituents in the outer layer; if these are chlorine atoms carrying a negative charge they will be easily detached and form negative chlorine atoms and the compound will be, as Werner showed it is, an electrolyte, with ions  $\text{PtCl}_2(\text{NH}_3)_2$  and  $\text{Cl}^- \text{Cl}^-$ . The work required to separate the ions  $\text{PtCl}_2(\text{NH}_3)_2^+$  comes from the loss of potential energy due to the approach of the polar molecules to the central system, and not from thermal agitation. The reasons in favour of this view of electrolytic dissociation are in my opinion very strong. I have already pointed out that to ionise a molecule isolated from other molecules would require an amount of energy comparable with the "ionising potential" of one of its atoms, a quantity varying from one element to another, but comparable with 10 volts. As the average kinetic energy of a molecule at  $0^\circ \text{C}$ . due to thermal agitation is, when measured on the same scale, only about  $1/30$  of a volt, it will be seen that there is little likelihood of the ionisation being due to thermal agitation.

On this view of electrolytic dissociation the ions in the solution are not simple atoms or radicles, but combinations of these with polar molecules. These molecules not only dissociate the original molecule, but after dissociation they tend to keep the ions apart. They surround the charge on the central atom with an oppositely charged layer and thus diminish its attraction on other systems. Thus, for example, in an aqueous solution of  $\text{CaCl}_2$  the positively electrified part of the calcium atom would have next to it the negative ends of polar water molecules, and the attraction between it and an oppositely charged chlorine atom would be diminished. The researches of Mr. Washburn furnish direct experimental evidence of the hydration of ions.<sup>17</sup>

(To be continued.)

---

**On the Production of Colored Flames for Use with Spectrometers and Polarimeters.** J. J. MANLEY. (*Phil. Mag.*, Feb., 1923.)—From the laboratory of Magdalen College, Oxford, comes this method of feeding the solution through a bunch of platinum wires into the flame. It seems to be a boon to physicists for "It is extremely convenient, requires but little attention and by its means an intense flame coloration can be maintained for any desired period." In addition it can be made by the experimenter. G. F. S.

---

<sup>17</sup> *Technology Quarterly*, 21, p. 288 (1908).



**Hendricus Gerardus van de Sande Bakhuyzen**, the Dutch astronomer, died on January 8, 1923. He was born in the Hague in 1838. After having been professor of physics in the Polytechnic School in Delft, he became professor of astronomy at the University of Leiden and director of the observatory. Under his direction a catalog of more than 10,000 stars was made. He worked with Gill, the Cape of Good Hope astronomer, to determine the amount of astronomical refraction. His study of changes of the mean level of the sea on the Dutch coast contributed to the explanation of variation of latitude. The period of the rotation of Mars was determined by him to a fraction of a second. Outside of his chosen field, he had a large part in the publication of the monumental edition of the works of Huyghens and he further served as secretary of the International Society of Geodesy. (*Comptes Rendus*, Jan. 22, 1923.)

G. F. S.

**Spectra of Hydrogen, Nitrogen and Oxygen in the Extreme Ultra-violet.** J. J. HOPFIELD. (*Phys. Rev.*, Dec., 1922.)—"It had long been assumed by investigators in the extreme violet, that most gases, and especially oxygen, are opaque in this region." Certain previous experiments made by this author had led him to doubt this. His present paper shows that he was correct. He used a vacuum grating spectrograph, specially prepared photographic plates and an oil-cooled discharge tube capable of standing an input of 2.25 KW. All three gases were found to transmit light of wave-length 1100 to 1225 Ångstrom units even when the pressure was as high as 3 cm. In oxygen at .001 mm. pressure its spectrum was photographed down as far as 430 units. The wave-lengths of 100 new oxygen lines are given, obtained with the disruptive discharge. Fifty new nitrogen lines are also given.

G. F. S.

**The Early Stages of a Submarine Explosion.** (*Phil. Mag.*, Feb., 1923.)—Gas is supposed to be set free in an instant in a spherical cavity situated in a limitless mass of liquid assumed to be incompressible. If the diameter of the cavity is at first one metre and the initial pressure of the gas 1000 atmospheres, then in water the diameter doubles in  $\frac{1}{2\sqrt{50}}$  sec. and grows to 5 metres in about  $\frac{1}{30}$  sec. The maximum speed with which the limits of the cavity travel outward is 145 m. per sec., nearly one-tenth of the speed of sound in water. If the initial pressure had been 10,000 atmospheres, the doubling and the quintupling of the diameter would occur in respectively  $\frac{1}{7\sqrt{50}}$  and  $\frac{1}{100}$  sec., while the maximum outward speed would be 460 m. per sec.

The compressibility of water will, of course, modify these data, though to no great extent, until pressures of the order of 10,000 atmospheres are introduced. "The accurate equations of motions of spherical waves are easily formulated, although a solution seems at present hopeless."

G. F. S.



# ILLUSTRATIONS OF ELECTRIC DISPLACEMENT CURRENTS.\*

BY

JOSEPH S. AMES, Ph.D., LL.D.

Director of Physical Laboratory, The Johns Hopkins University, Baltimore, Maryland;  
Associate Editor of this JOURNAL, Member of the Institute.

THIS note contains a method of discussing displacement currents which is perfectly obvious and yet which, so far as I can learn, is not given in any text-book on electricity; and also a few illustrations.

If  $\epsilon$  is the dielectric constant of a homogeneous isotropic dielectric and  $\bar{E}$  the intensity of the electric field at any point in it due to any distribution of stationary charges, the electric displacement  $\bar{D}$  at that point is defined by the equation  $\bar{D} = \frac{\epsilon}{4\pi} \bar{E}$ . Maxwell introduced the concept of a displacement current, whose value per unit cross-section is defined to be  $\frac{\partial \bar{D}}{\partial t}$ , and discussed the continuity of the vector sum of the conduction current density  $\bar{j}$  and  $\frac{\partial \bar{D}}{\partial t}$ . Later, as a consequence of Rowland's experiments on convection of electric charges and the resulting idea of convection currents, FitzGerald showed that  $\bar{j} = \frac{\partial \bar{D}}{\partial t} + \rho \bar{v}$ , where  $\rho$  is the volume density of charge and  $\bar{v}$  is its velocity, was the vector to be considered as the total current density. Various authors have shown, therefore, that this vector is to be considered as solenoidal.

As the simplest illustration of displacement currents, those due to a point charge  $e$  moving with a "slow" velocity  $v$  may be considered. Since this problem is obviously one of axial symmetry, the axis of  $X$  may be chosen as the direction of the velocity and that of  $Y$  any line perpendicular to this. An observer moving with the charge would observe in the space around him a potential  $\varphi = \frac{e}{\epsilon r}$ , and values of the electric intensity whose components  $E_x = -\frac{\partial \varphi}{\partial x}$ ,  $E_y = -\frac{\partial \varphi}{\partial y}$ ,  $E_z = 0$ . An observer, stationary in space, will note the same values, provided the velocity of the charge is

---

\* Communicated by the Author.



so slow that the electric intensity  $\frac{1}{v} [v.H.]$  may be neglected. To this latter observer the displacement current density will have the components  $\frac{\partial D_x}{\partial t} = \frac{\epsilon}{4\pi} \frac{\partial E_x}{\partial t}$  and  $\frac{\partial D_y}{\partial t} = \frac{\epsilon}{4\pi} \frac{\partial E_y}{\partial t}$ . But  $\frac{\partial}{\partial t} = -v \frac{\partial}{\partial x}$ , where  $x$  is the coördinate of the point in question with reference to axes moving with the charge. Therefore

$$i_x = \frac{\partial D_x}{\partial t} = -\frac{\epsilon}{4\pi} v \frac{\partial E_x}{\partial x};$$

$$i_y = \frac{\partial D_y}{\partial t} = -\frac{\epsilon}{4\pi} v \frac{\partial E_y}{\partial x}$$

A stationary doublet of strength  $ve$ , consisting of charges  $+\frac{e}{\alpha}$  and  $-\frac{e}{\alpha}$  at a distance  $\alpha v$  apart, where  $\alpha$  is an infinitesimal number, whose axis is taken as the axis of  $X$ , produces a field of displacement whose components at any point are

$$\frac{\epsilon}{4\pi} \left\{ E'_x - \left( E'_x + \frac{\partial E'_x}{\partial x} \alpha v \right) \right\} = -\frac{\epsilon}{4\pi} \alpha v \frac{\partial E'_x}{\partial x} \quad \text{and}$$

$$\frac{\epsilon}{4\pi} \left\{ E'_y - \left( E'_y + \frac{\partial E'_y}{\partial x} \alpha v \right) \right\} = -\frac{\epsilon}{4\pi} \alpha v \frac{\partial E'_y}{\partial x}$$

The  $E'_x$  and  $E'_y$  in these expressions are the components of the electrical intensity due to a charge  $\frac{e}{\alpha}$ ; in the formulas for  $i_x$  and  $i_y$ ,  $E_x$  and  $E_y$  refer to a charge  $e$ ; therefore  $E'_x = \frac{1}{\alpha} E_x$ ;  $E'_y = \frac{1}{\alpha} E_y$ . Finally, the field of displacement due to the stationary doublet of strength  $ve$  has for its components  $-\frac{\epsilon}{4\pi} v \frac{\partial E_x}{\partial x}$  and  $-\frac{\epsilon}{4\pi} v \frac{\partial E_y}{\partial x}$ , identically the same as the components of the displacement current density due to a charge  $e$  having a velocity  $v$ .

This theorem may be generalized: Let there be any distribution of charges,  $\rho$ ,  $\sigma$  or  $e$ , which has a uniform velocity  $\bar{v}$ ; the displacement current density produced thereby is identically the same as the displacement due to a stationary polarized distribution formed by associating with  $\frac{\rho}{\alpha}$ ,  $\frac{\sigma}{\alpha}$  or  $\frac{e}{\alpha}$  charges of opposite signs at a distance  $\alpha v$  in a direction opposite to that of the original motion. This fact enables one to draw the lines of the displacement current density immediately, if the corresponding lines of displacement are known.



## ILLUSTRATIONS.

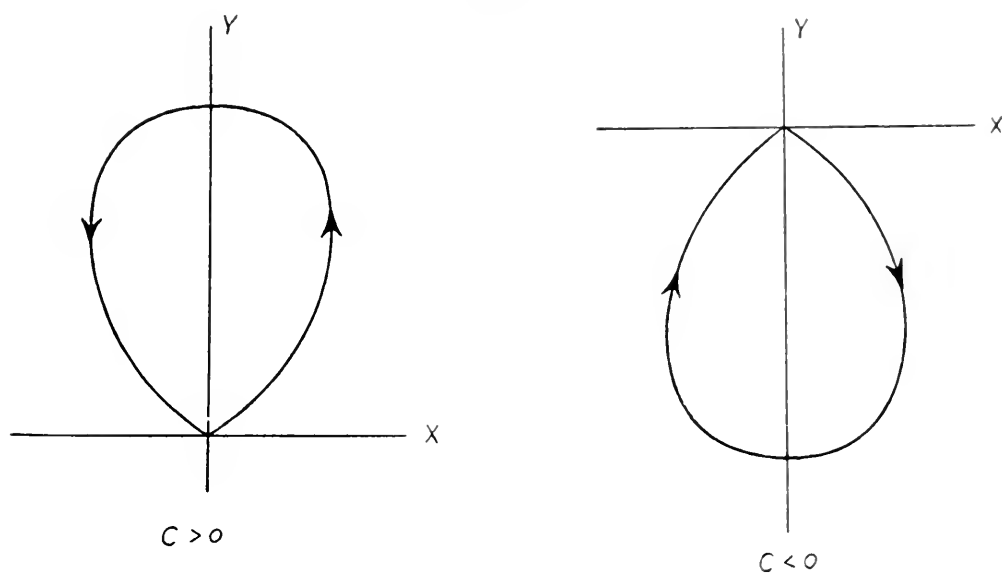
1. A charge  $e$  has a velocity  $v$  along the axis of  $X$ . The curves for the displacement current—with reference to axes moving with the charge—are the same as those of the displacement due to a doublet of strength  $ev$ , with its axis along the axis of  $X$ .

The direct proof is as follows:

$$\varphi = \frac{e}{\epsilon r}; E_x = -\frac{\partial \varphi}{\partial x} = \frac{ex}{\epsilon r^3}; E_y = \frac{ey}{\epsilon r^3}.$$

$$i_x = -\frac{\epsilon v}{4\pi} \frac{\partial E_x}{\partial x} = \frac{ve}{4\pi} \frac{2x^2 - y^2}{r^5}; i_y = \frac{ve}{4\pi} \frac{3xy}{r^5}$$

FIG. 1.



Hence the differential equation of the curves is

$$\frac{dy}{dx} = \frac{3xy}{2x^2 - y^2}$$

the solution of which is  $(x^2 + y^2)^{3/2} = Cy^2$  or, in polar coördinates  $r = C \sin^2 \vartheta$ , i.e., the well-known equation for the lines of displacement due to a doublet.

Typical curves for  $C > 0$  and  $C < 0$  are shown in Fig. 1. Each "tube" of displacement current has an infinitesimal gap at the origin which is closed by the *convection* current due to the moving charge; so that the vector  $\frac{\partial D}{\partial t} + \rho \vec{v}$  is solenoidal.

This solenoidal condition may be explained more in detail. Let the moving charge  $e$  be distributed uniformly through a sphere of radius  $R$ , so that  $e = \frac{4}{3} \pi R^3 \rho$ . For points *outside* the sphere



the tubes of displacement current are the same as those of displacement due to a doublet of strength  $ev$  placed at the centre, *i.e.*,  $i_x = \frac{ev}{4\pi} \frac{2x^2 - y^2}{r^5}$ ,  $i_y = \frac{ev}{4\pi} \frac{3xy}{r^5}$ . For points *inside* the sphere  $E_x = \frac{4}{3} \frac{\pi \rho x}{\epsilon}$ ,  $E_y = \frac{4}{3} \frac{\pi \rho y}{\epsilon}$  and therefore  $i_x = -v \frac{\epsilon}{4\pi} \frac{\partial E_x}{\partial x} = -\frac{v}{3} \rho$  and  $i_y = 0$ . In addition, there is a convection current inside of density  $\rho v$  in the direction of the  $X$  axis. At the surface the normal component of the current density outside is  $i_x \cos \vartheta + i_y \sin \vartheta = \frac{evx}{2\pi R^4}$ , and inside it is  $\frac{3}{2} v \rho \cos \vartheta = \frac{evx}{2\pi R^4}$ .

If one wishes to consider total currents, rather than current densities, describe an infinite plane through the centre of the sphere perpendicular to the axis of  $X$ . Through all points of this outside the sphere there is a displacement current, in a direction opposite to  $\bar{v}$ , of density  $\frac{ev}{4\pi} \frac{y^2}{r^5} = \frac{ev}{4\pi} \frac{1}{r^3}$ . Therefore the total displacement current is  $\int_R^\infty \frac{ev}{4\pi} \frac{1}{r^3} 2\pi r dr = \frac{ev}{2R}$ . Across this same plane inside the sphere there is a displacement current density  $\frac{v}{3} \rho$  in a direction opposite to  $\bar{v}$  and a convection current density  $\rho v$  in the direction of  $\bar{v}$ , therefore a total current density in the direction of  $\bar{v}$  of  $\frac{2}{3} \rho \bar{v}$ . So the total current in this direction inside the sphere is  $\frac{2}{3} \rho \bar{v} \cdot \pi R^2$ . But  $\rho = \frac{3}{4} \frac{e}{\pi R^3}$ ; therefore this total current is  $\frac{ev}{2R}$ , continuous with the displacement current outside the sphere. All of what has just been proved holds equally well if the dielectric of the sphere through which the charge is uniformly distributed is different from the dielectric outside.

It may not be without interest to note that even in this latter case the electromagnetic force on the sphere produced when the charge is moving through a uniform magnetic field is due to the convection current only. According to Ampère's law, the force acting on an element  $ds$  of conduction current  $J$  when placed in a magnetic field of intensity  $H$  is  $\mu \frac{J}{c} [\bar{ds}, \bar{H}]$ . In the case of the moving sphere, let the magnetic field be at right angles to the line of motion. The total convection current through an element of an equatorial plane perpendicular to the line of motion is  $\rho v \cdot 2\pi y dy$ ; its length inside the sphere is  $2x$ ; therefore the force on the whole



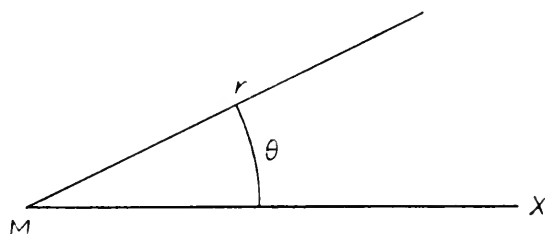
sphere is  $\frac{\mu}{c} H \int_0^R \rho r' \cdot 2\pi y \cdot 2x \cdot dy = \frac{\mu}{c} \frac{4}{3} \pi \rho R^3 x H = \frac{\mu}{c} c x H$ , the well-known value. Consequently, the displacement current inside the sphere, of density  $-\frac{1}{3} \rho r'$ , as appears to a stationary observer, does not contribute to this force.

2. A doublet of strength  $M$  has a velocity  $\bar{v}$  in the direction of its axis. This is again a case of axial symmetry.

The curves for the displacement current are the same as those of the displacement for the combination of a doublet of strength  $\frac{M}{\alpha}$  and one of strength  $-\frac{M}{\alpha}$  displaced in the opposite direction to  $\bar{v}$  by an amount  $\alpha \bar{v}$ .

The direct proof is as follows (Fig. 2) :

FIG. 2.



$$\phi = \frac{M \cos \theta}{\epsilon r^2} = \frac{Mx}{\epsilon r^3}$$

$$E_x = -\frac{\partial \phi}{\partial x} = \frac{3Mx^2}{\epsilon r^5} - \frac{M}{\epsilon r^3}; \quad E_y = \frac{3Mxy}{\epsilon r^5}$$

$$i_x = -v \frac{\epsilon}{4\pi} \frac{\partial E_x}{\partial x} = \frac{v}{4\pi} \left( \frac{15Mx^3}{r^7} - \frac{9Mx}{r^5} \right);$$

$$i_y = -\frac{v\epsilon}{4\pi} \frac{\partial E_y}{\partial x} = \frac{v}{4\pi} \left( \frac{15Mx^2y}{r^7} - \frac{3My}{r^5} \right)$$

$$i_x = \frac{v}{4\pi} \frac{3Mx}{r^7} (2x^2 - 3y^2); \quad i_y = -\frac{v}{4\pi} \frac{3My}{r^7} (4x^2 - y^2).$$

Hence the differential equation of the curves for the displacement current is  $\frac{dy}{dx} = \frac{y}{x} \frac{4x^2 - y^2}{2x^2 - 3y^2}$ ; the solution of which is  $(x^2 + y^2)^{1/2} = Cxy^2$ ; or, expressed in polar coördinates,  $r^2 = C \cos \theta \sin^2 \theta$ . This is the well-known equation for the combination of doublets referred to previously.

Typical curves for  $C > 0$  and  $C < 0$  are shown in Fig. 3.

For  $C = \infty$ ,  $x = 0$  and  $y = 0$ .

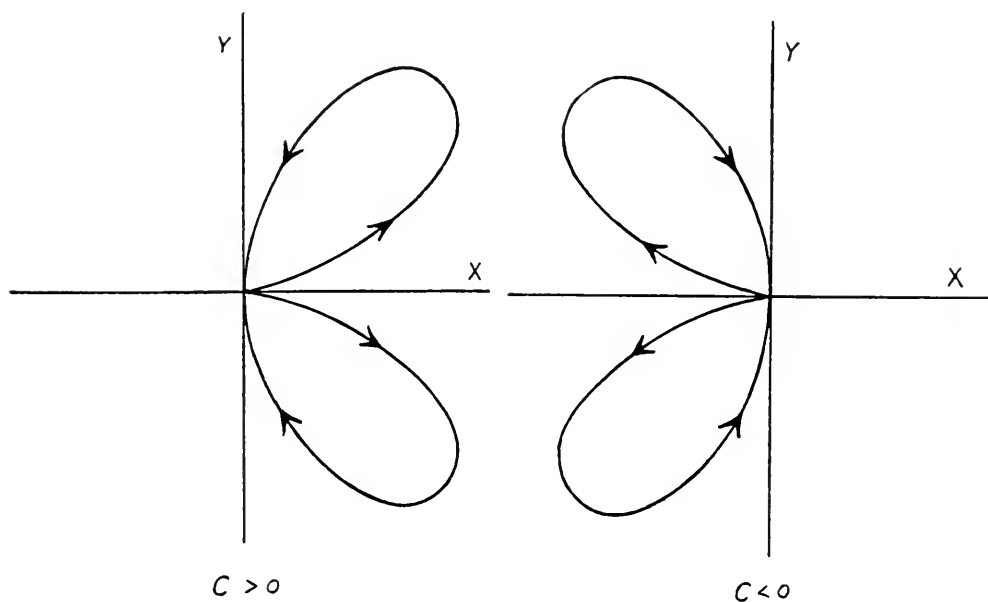


At all points along the lines  $2x = \pm y$ , the curves are parallel to the  $X$  axis, etc.

At the origin each curve has an infinitesimal "gap" which is closed by the convection current due to the moving doublet. All the curves for  $C > 0$  are closed by the convection current due to the moving plus charge of the doublet, while the curves for  $C < 0$  are closed by the motion of the negative charge.

This solenoidal condition may be described more in detail. Let the doublet be considered as a polarized sphere of radius  $R$ ,

FIG. 3



the strength  $M$  being equal to  $eh$ . The following quantities must be calculated:

(a) Displacement current density, in dielectric immediately outside the sphere. From what has just been proved

$$i_{x_1} = \frac{3Mv}{4\pi R^7} x(2x^2 - 3y^2); \quad i_{y_1} = \frac{3Mv}{4\pi R^7} y(4x^2 - y^2)$$

(b) Displacement current density in the surface layer of the sphere. A simple calculation gives for this

$$i_{x_2} = -\frac{3ev}{4\pi R^5} x^2 + \frac{3Mvx}{4\pi R^7} (2x^2 - 3y^2); \quad i_{y_2} = -\frac{3ev}{4\pi R^5} xy + \frac{3Mv}{4\pi R^7} y(4x^2 - y^2)$$

(c) Convection current density in surface layer

$$i_{x_3} = \rho v = \frac{3ev}{4\pi R^3}; \quad i_{y_3} = 0$$

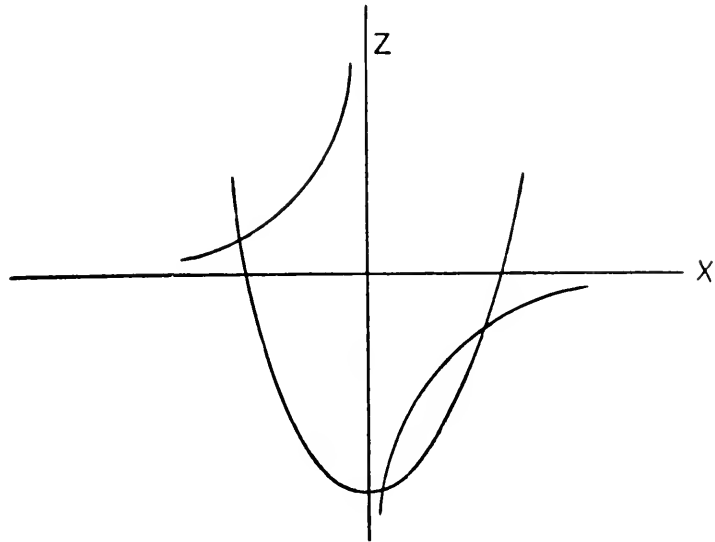


N. B.—In the spherical space enclosed by the surface layer,  $E$  is uniform; hence  $\frac{\partial \bar{D}}{\partial t} = 0$ .

It is seen that  $i_{x_2}$  and  $i_{y_2}$  are made up of two terms; the second ones are identical with  $i_{x_1}$  and  $i_{y_1}$ ; and the first ones are components of a vector  $-\frac{3\bar{v}}{4\pi R^3} \frac{x}{R}$ , normal to the surface, which is equal and opposite to the normal component of  $i_{x_3}$ . Consequently the normal component of the vector  $\frac{\partial \bar{D}}{\partial t} + \rho \bar{v}$  is continuous through the surface.

The mechanism then of the total current is as follows: Outside

FIG. 4.



the sphere there is a flux of current away from the part of the surface near the axis, which returns again to the “ polar ” part of the surface; this current is continuous with and supplied by that part of the displacement current inside the surface layer due to the second terms in  $i_{x_2}$  and  $i_{y_2}$ ; this current in turn is supplied by the tangential component of the convection current in the surface layer. Or, considered more simply, each tube of displacement current outside the sphere carries away a certain current from the surface where it starts and returns it to the surface where it ends, and this current is carried back to its starting point by the convection current in the surface.

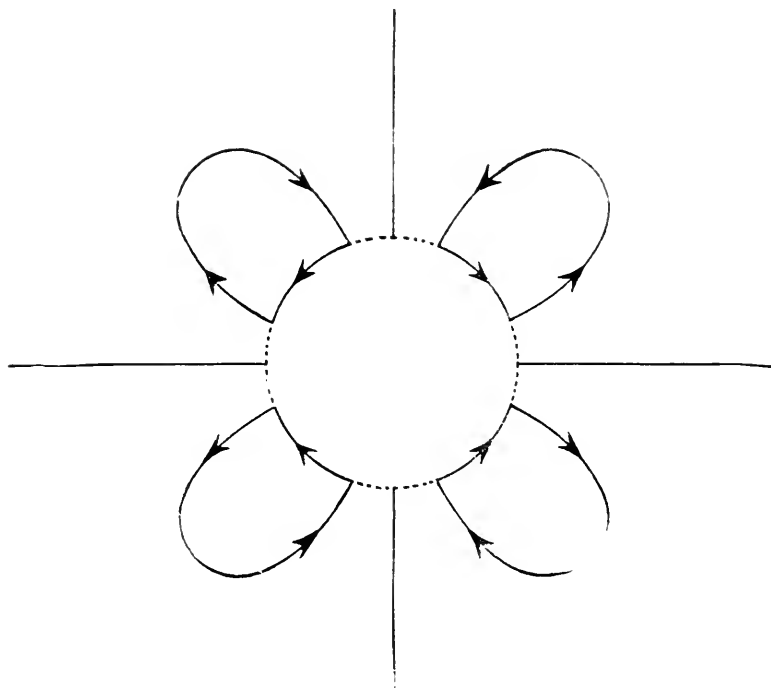


The total flux of current may be calculated. The current density immediately outside the sphere has the components

$$i_x = \frac{3Mv}{4\pi R^7} x(2x^2 - 3y^2); \quad i_y = \frac{3Mv}{4\pi R^7} y(4x^2 - y^2)$$

and therefore the radial component  $i_r = \frac{3Mv}{4\pi R^6} (2x^2 - y^2) = \frac{3Mv}{4\pi R^4} (3 \cos^2 \vartheta - 1)$ . This component vanishes when  $3 \cos^2 \vartheta - 1 = 0$ , i.e., when  $\vartheta = \cos^{-1} \sqrt{\frac{1}{3}}$ . This critical angle, which may be

FIG. 5.



called  $\vartheta_0$ , denotes a certain point on the sphere such that for values of  $\vartheta < \vartheta_0$  there is a current flux away from the sphere, and for values of  $\vartheta > \vartheta_0$  the flux is returning to the sphere. The total flux away from the "axial cap" of the sphere is therefore

$$\int_0^{\vartheta_0} \frac{3Mv}{4\pi R^4} (3 \cos^2 \vartheta - 1) \cdot 2\pi R^2 \sin \vartheta \, d\vartheta = \frac{Mv}{R^2} \cos \vartheta_0$$

and there is, of course, an equal flux back to the sphere. (The same conditions prevail at the opposite axial cap of the sphere.)

The tangential component of the convection current density in the surface layer is  $\rho v \sin \vartheta = \frac{3ev}{4\pi R^3} \sin \vartheta$  and is directed towards the axis. It flows through a surface, perpendicular to the tangent,



of area  $h \cos \vartheta \cdot 2\pi R \sin \vartheta$ ; therefore the current flux is  $\frac{3eh}{2R^2} v \cos \vartheta \sin^2 \vartheta$ . But  $eh = \bar{M}$ , and hence this flux at any angle  $\vartheta$  is  $\frac{3Mv}{2} \cos \vartheta \sin^2 \vartheta$ . Its maximum value is for  $\cos^2 \vartheta = \frac{1}{3}$ , i.e., at  $\vartheta_0$ , because at this angle the current is the sum of all the partial currents, each of which joins the two open ends of a tube of current flowing outside the sphere. The total convection current, corresponding to the total flux of displacement current away from the sphere and back to it, is found by making  $\vartheta = \vartheta_0$ ; this is  $\frac{Mv}{R^2} \cos \vartheta_0$ . This is simply a consequence of the proof previously given that the vector  $\frac{\partial \bar{D}}{\partial t} + \rho \bar{v}$  is solenoidal.

It may be of interest to investigate the intersections of any one curve  $r^5 = C xy^2$ , e.g., one for which  $C > 0$ , with a circle of radius  $R$  described around the origin. On substitution, the equation for  $x$  is

$$x^3 - xR^2 = -\frac{R^5}{C}$$

This may be discussed graphically by drawing the hyperbola  $xz = -\frac{R^5}{C}$  and the parabola  $x^2 - z = R^2$ . (Fig. 4.) It is seen at once that there is always one real intersection of these curves, for a positive value of  $z$ ; but  $y^2 = -z$ , and therefore, although  $x$  is real,  $y$  is imaginary. The other two intersections may be real or imaginary. They will coincide when the original equation for  $x$  has two equal roots, i.e., when  $x^2 = \frac{R^2}{3}$ ,  $x^3 = \frac{R^5}{2C}$ , or when  $R^2 = \frac{2}{3} \sqrt{\frac{1}{3} C}$ . This gives the radius of the circle which circumscribes the original curve for a definite value of  $C$ . (The point of tangency of the circle and curve has, obviously, the coördinates  $\sqrt{\frac{1}{3}} R$  and  $\pm \sqrt{\frac{2}{3}} R$ , or  $R$  and  $\cos^2 \vartheta = \frac{1}{3}$ .) For values of  $R$  less than this critical one, the lower branch of the hyperbola has two real intersections, for each of which  $z$  is negative and therefore  $y$  is real. For values of  $R$  greater than this critical value, the two intersections are imaginary, and therefore  $y$  is imaginary. Summary: The intersections of the circle of radius  $R$  with the curve  $r^5 = C xy^2$  are given as follows in terms of the radius of the circumscribing circle  $R_0$ .

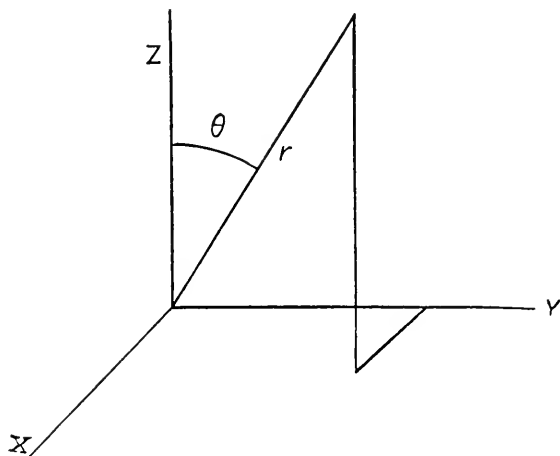


- (1)  $R < R_0$ ,  $x$  has 3 real roots,  $\pm y$  has 2 real values, 1 of which is imaginary; therefore there are 4 points of intersection.
- (2)  $R = R_0$ ,  $x$  has 3 real roots, 2 of which coincide, etc.; condition of tangency.
- (3)  $R > R_0$ ,  $x$  has 1 real root and 2 imaginary ones; all values of  $y$  are imaginary; therefore there is no intersection in real points.

3. An uncharged dielectric or conducting sphere moves with a velocity  $\bar{v}$  in and parallel to a uniform field of force.

When such a sphere of radius  $R$  is in a uniform field of force of intensity  $\bar{E}$ , the field at points outside the sphere is modified

FIG. 6.



by the addition of a field due to a doublet of strength  $M = \alpha R^3 E$  placed at the centre of the sphere with its axis parallel to the field. (For a conductor  $\alpha = 1$ , for a dielectric  $\alpha < 1$ .) Inside the sphere the field is uniform or zero. When the sphere is moving, therefore, in the direction of the field, there is no change at a point inside the sphere, *i.e.*, there is no displacement current inside; and, for points outside the sphere, the displacement currents are simply those due to a moving doublet, as given in the previous illustration.

A typical set of curves is then as shown in Fig. 5. Each branch of each curve is closed by the current along the surface of the sphere, due to the component of the velocity tangent to the sphere of the apparent or real charge of surface density  $P_n$  or  $\sigma$ .

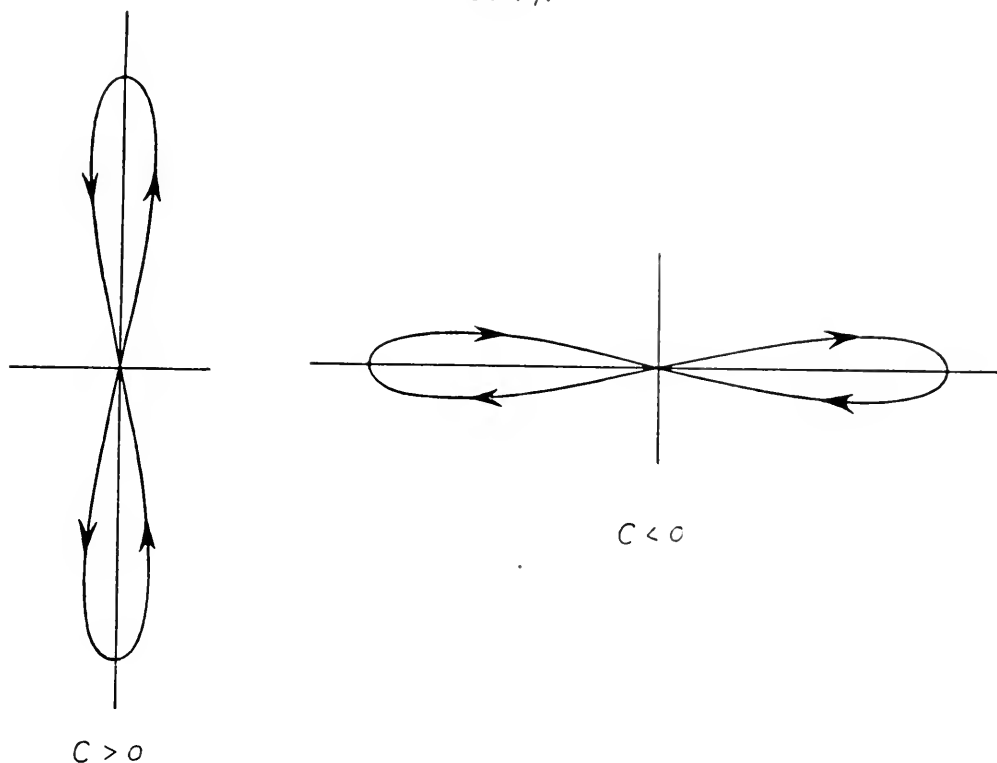


4. A doublet of strength  $M$  has a uniform velocity  $\bar{v}$  at right angles to its axis.

In the previous cases there was axial symmetry, but not in this.

Choose the  $Z$  axis as that of the doublet, and the  $Y$  axis as that of the velocity. (Fig. 6.)

FIG. 7.



$$\varphi = \frac{M \cos \vartheta}{\epsilon r^2} = \frac{Mz}{\epsilon r^3}$$

$$E_x = \frac{3Mxz}{\epsilon r^5}; \quad E_y = \frac{3Myz}{\epsilon r^5}; \quad E_z = \frac{3Mz^2}{\epsilon r^5} - \frac{M}{\epsilon r^3}$$

$$-\frac{\partial E_x}{\partial y} = \frac{15Mxyz}{\epsilon r^7}; \quad -\frac{\partial E_y}{\partial y} = \frac{15My^2z}{\epsilon r^7} - \frac{3Mz}{\epsilon r^5};$$

$$-\frac{\partial E_z}{\partial y} = \frac{15Myz^2}{\epsilon r^7} - \frac{3My}{\epsilon r^5}$$

Hence the differential equation of the displacement current curves is given by

$$\begin{aligned} dx: dy: dz &= 5xyzr^{-2} : z(5y^2r^{-2} - 1) : y(5z^2r^{-2} - 1) \\ &= 5xyz : z(4y^2 - x^2 - z^2) : y(4z^2 - x^2 - y^2) \end{aligned}$$



Therefore, in the  $Y - Z$  plane, the equation of the curves is

$$\frac{dy}{dz} = \frac{z(4y^2 - z^2)}{y(4z^2 - y^2)}$$

The solution of which is

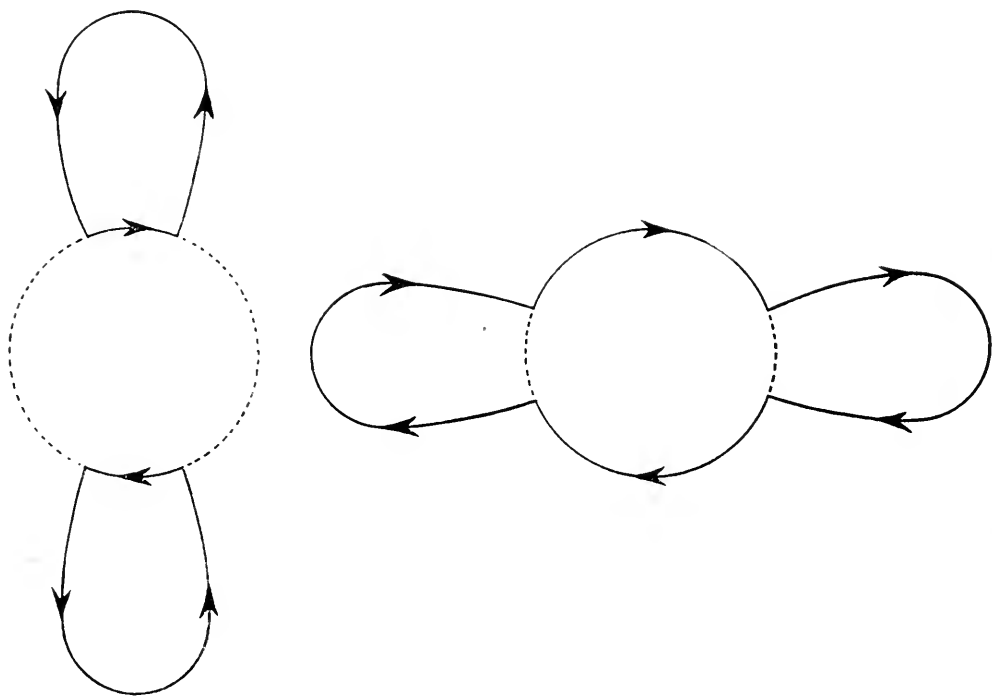
$$(z^2 + y^2)^{5/3} = C(z^2 - y^2)$$

or  $r^{4/3} = C \cos 2\theta$ .

Typical curves for  $C > 0$  and  $C < 0$  are shown in Fig. 7.

For  $C = \infty$ ,  $z^2 - y^2 = 0$ , or  $z - y = 0$  and  $z + y = 0$ .

FIG. 8.



The continuity of the curves at the origin is maintained by the convection currents due to the motion of the positive and negative charges making up the doublet.

Considering the doublet as due to a sphere polarized in the direction of the  $Z$  axis, and drawing typical curves for  $C > 0$  and  $C < 0$  in the  $Y - Z$  plane, together with the convection currents which makes these curves continuous, it is seen that they are as shown in Fig. 8.



# THE ACOUSTICS OF ROOMS.

## REVERBERATIONS.\*

BY

E. A. ECKHARDT, Ph.D.

Physicist, Bureau of Standards, Member of the Institute.

THE problem of architectural acoustics like those of traffic regulation and of transportation generally has become acute because of the industrial developments of recent decades. The increasing use of concrete and of fire-proof construction has confronted us with acoustical horrors, the like of which were probably unknown to our forefathers. The attempts to understand and to mitigate this situation were little more than stabs in the dark until the genius of Professor Sabine brought order into the chaos of speculation that had previously existed. Some twenty odd years have passed since Professor Sabine's results have been available and even to-day rooms with poor acoustical features are being built in large numbers. Some of these receive remedial treatment; others remain a continual source of irritation to those who are obliged to use them.

The question arises whether reasonably satisfactory acoustical conditions can now be assured in advance of construction. This can be answered in the affirmative. Some architects secure satisfactory acoustical results consistently. Then why is it not done more generally? Probably because many architects find it difficult to understand and to utilize the data which the researches of physicists have made available. A few physicists are assisting architects with their acoustical problems. More coöperation of this kind will help make each room acoustically satisfactory to the extent of our present knowledge. Further research will enable us to do much better in the future.

The most important difficulty encountered in public assembly rooms is that of reverberation. One of its annoying manifestations is the persistence of a sound in the room after the sound source has ceased to emit. Because of reverberation the sound heard at any moment by the individuals of an audience is due not

---

\* Presented at the Stated Meeting of the Institute held Wednesday, January 17, 1923.



to a single syllable uttered by the speaker, but to a number of consecutive syllables, and this necessarily leads to confusion.

In order to know how this confusion may be eliminated, it is necessary to determine just how it arises.

If somewhere in a closed room we begin to emit sound at a constant rate, the nearest surface will be the first to reflect, and an appreciable time will elapse before the remotest surface participates in the reflection, this time being longer the larger the room. For every quantity of sound energy  $E$  incident on the walls a definite fraction  $a$  is absorbed on the average. With advancing time the quantity of sound energy which falls upon the surfaces of the room will increase and consequently the rate of absorption by the walls will grow until it equals the rate of emission by the source. When this condition is reached the average sound intensity in the room has a maximum value, which will be maintained as long as the sound emission continues unchanged.

If now the sound emission is stopped, the sound intensity will gradually diminish until all the energy has been absorbed by the surfaces of the room. The rate of absorption is always proportional to the amount of energy present and the sound intensity therefore falls off at a progressively decreasing rate.

But a qualitative consideration of the situation, while helpful, is not sufficient for practical purposes. We shall find it profitable to derive formulas, describing the growth and decay of sound intensity in a room and to use them in our further consideration of the reverberation problem. Such formulas have been developed by Jaeger.<sup>1</sup> A hitherto unpublished derivation of these equations by Buckingham has several advantages which commend it for our use. Buckingham considers the sound energy divided up into a very large number of equal parts and assumes that in the steady state, when the sound intensity is stationary, these energy units are uniformly distributed throughout the room, both with respect to position and to direction of motion. These assumptions, which are the same as those made by Jaeger, ignore the existence of interferences and the equations which follow are valid only to the extent to which interference phenomena may be ignored. All the energy units are of course moving with a constant speed, that of sound.

---

<sup>1</sup>Jaeger, G., "Zur Theorie des Nachhalls," *Wiener Sitzungsberichte*, 120, May, 1911.



We shall consider an element of volume  $dV$  anywhere in the room and an element of surface  $ds$  also chosen at random. The distance from the centre of the volume element to the centre of the surface element we shall denote by  $r$ . If  $N$  is the number of energy units per unit volume, the volume  $dV$  will contain  $NdV$  such units. If  $d\omega$  is the solid angle subtended at the volume element by  $ds$  the number of energy units in  $dV$  which are moving in direction which pass through  $ds$  is  $NdVd\omega/4\pi$ . If  $\theta$  is the angle between the normal to the surface element  $ds$  and the direction  $r$  we may write  $d\omega = ds \cos \theta / r^2$ . The number of energy units in  $dV$  which will ultimately pass through  $ds$  is, therefore, given by

$$\frac{NdVds \cos \theta}{4\pi r^2} \quad (1)$$

If  $dV$  is taken to include the space between  $r$  and  $r + dr$  and  $\theta$  and  $\theta + d\theta$ , we may write

$$dV = 2\pi r \sin \theta \cdot r d\theta dr$$

and substituting in (1), the number of energy units which at any moment are contained in  $dV$  and which will ultimately reach  $ds$  is given by

$$\frac{1}{2} Ndsdr \sin \theta \cos \theta d\theta \quad (2)$$

For the whole hemispherical shell between  $r$  and  $r + dr$  this is

$$\frac{1}{2} Ndsdr \int_0^{\pi/2} \sin \theta \cos \theta d\theta = \frac{1}{4} Ndsdr \quad (3)$$

If we integrate with respect to  $r$  from  $r = 0$  to  $r = v$  = the velocity of sound, *i.e.*, over a hemisphere of radius  $v$  about  $ds$  as centre, we get the whole number of energy units that are moving toward the surface element  $ds$  and are near enough to reach it in one second.

The number of energy units reaching any bounding surface  $ds$  per unit time is, therefore,

$$\frac{1}{4} Nds \int_0^v dr = \frac{1}{4} Nvds \quad (4)$$

or if  $E$  = energy per unit volume, the energy incident upon any



finite surface area  $S$  per unit time is given by  $\frac{1}{4} EvS$  and that absorbed per unit time, by

$$a \frac{1}{4} EvS \quad (5)$$

where  $a$  = the coefficient of absorption peculiar to the area  $S$ . We may, therefore, at once write down the differential equation for the sound intensity in a closed room,

$$V \frac{\partial E}{\partial t} + \frac{1}{4} vaSE = A \quad (6)$$

where  $A$  = the rate of sound energy emission, assumed constant.

We shall find the solutions of equation (6) for the following special cases useful.

*A.* Uniform sound emission beginning at zero time. The solution for this case is

$$E = \frac{4A}{vaS} \left[ 1 - e^{-\frac{vaS}{4V}t} \right] \quad (7)$$

*B.* The steady state has been reached by uniform sound emission.

In this case  $\frac{\partial E}{\partial t} = 0$  and  $E = E_{\max}$ . Hence

$$E_{\max} = \frac{4A}{vaS} \quad (8)$$

*C.* Emission stopped after the steady state has been reached. Then  $A = 0$  and the solution for this case is

$$E = \frac{4A}{vaS} e^{-\frac{vaS}{4V}t} \quad (9)$$

or

$$E = E_{\max} e^{-\frac{vaS}{4V}t} \quad (10)$$

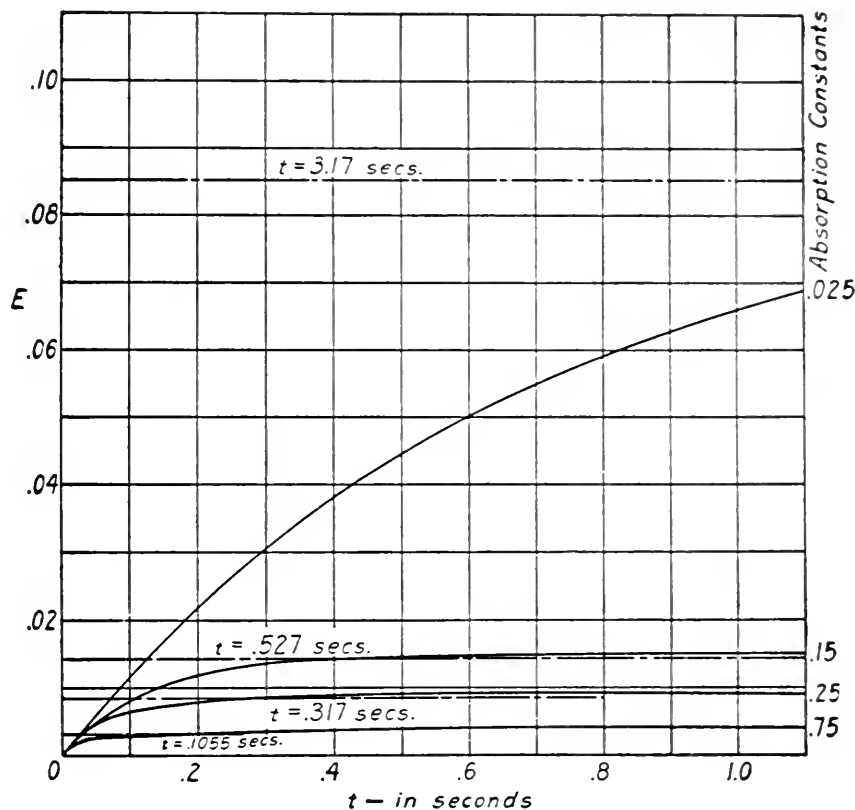
Equation (7) describes the growth of sound intensity in a room when sound is being emitted at a constant rate. The maximum intensity reached is given by equation (8). As far as properties of the room are concerned the maximum intensity is determined by the product  $a.S$ . This quantity was called by Sabine the absorbing power of the room. We conclude from equations (7) and (8) that the larger the absorbing power of the room the less intense will be the sound of a voice or a musical instrument. The volume of the room determines the intensity



only to the extent to which it determines the magnitude of the area  $S$ . Any changes in volume which can be made without changing the size and character of its surface areas will have no effect upon the absorbing power and hence upon the intensity.

It follows at once from equation (8) that for a given rate of sound emission the maximum intensity attained decreases as the absorbing power of the surfaces increases. This is shown graphically in Fig. 1 for a room of 1000 cubic metres volume.

FIG. 1.



Growth of sound intensity in a room for various degrees of absorption of its boundaries. The time values associated with the horizontal dot and dash lines give the time in which the intensity grows to 99 per cent. of the saturation value.

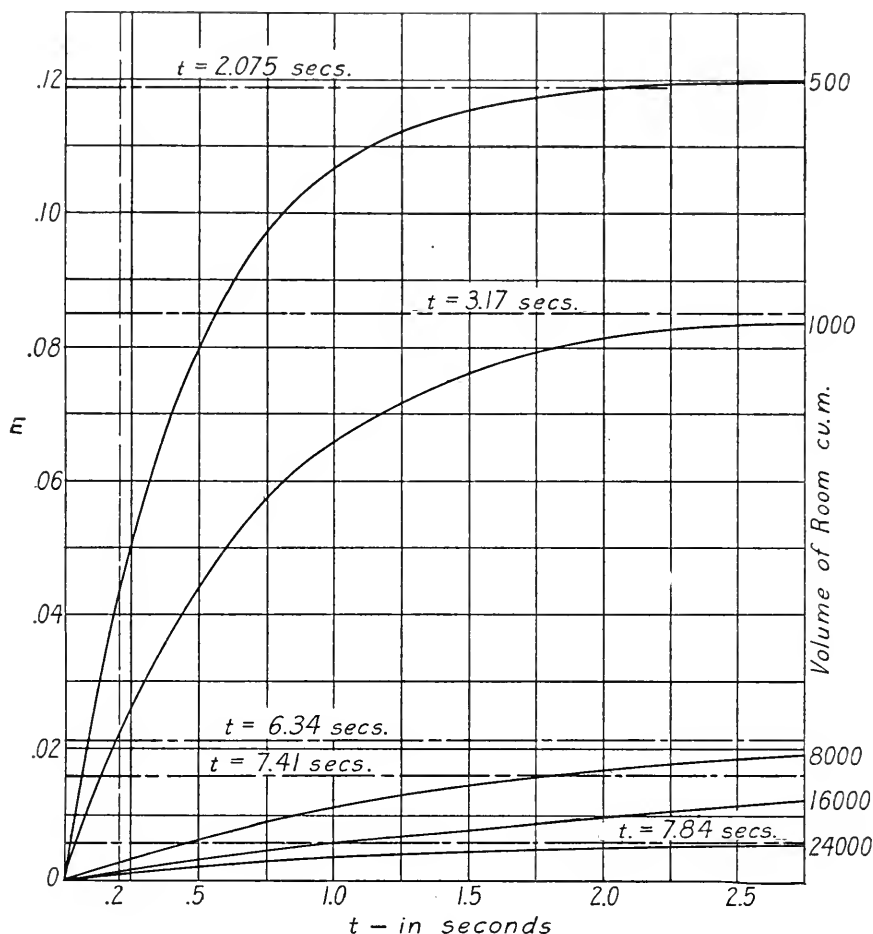
These curves cover the range from practically the smallest to the largest absorption coefficients actually realizable. For a small absorption coefficient the intensity rises slowly toward a large maximum. For a large absorption coefficient the intensity rises rapidly toward a relatively much smaller maximum.

On the other hand, the rate at which the intensity approaches its maximum is determined by the ratio  $aS/V$ . The maximum is reached the more quickly the larger this quantity. We shall see



later that this ratio has a preferred value.<sup>2</sup> In going to larger rooms the value of  $\frac{S}{V}$  necessarily decreases. In order to retain the preferred value of the ratio in this case  $\alpha$  must be increased in the ratio that  $\frac{S}{V}$  decreases. In other words, with increasing size the absorption per unit area of rooms must be increased in

FIG. 2.



Growth of sound intensity in rooms of different volumes, the boundaries being of the same poorly absorbing material in all cases.

order that satisfactory acoustical conditions may be assured. Failure to recognize this fact has led to a number of costly failures in the design of auditoriums.

In Fig. 2 are shown the sound intensity-growth curves for rooms of different volumes. The absorption constants were assumed the same for all of them. The curves indicate that for

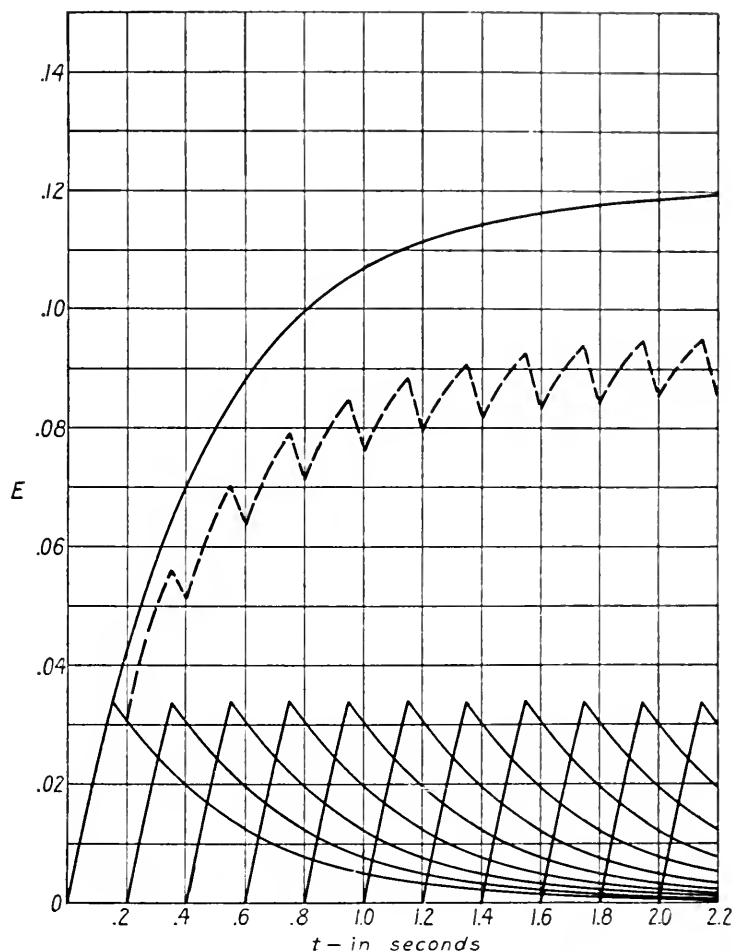
<sup>2</sup>The term optimum is avoided because the quantity has no mathematical maximum or minimum.



a given  $a$  the intensity rises more slowly the larger the room. The value of the rate of emission  $A$  in computing all the curves in this paper is that attributed to the average speaking voice.<sup>3</sup>

We shall now use the intensity-growth and decay equations in considering speech in a room, a case of discontinuous emission. In ordinary reading or speaking the average time interval per

FIG. 3.



Growth and decay of sound intensity for syllable emission in a room of too small absorbing power.

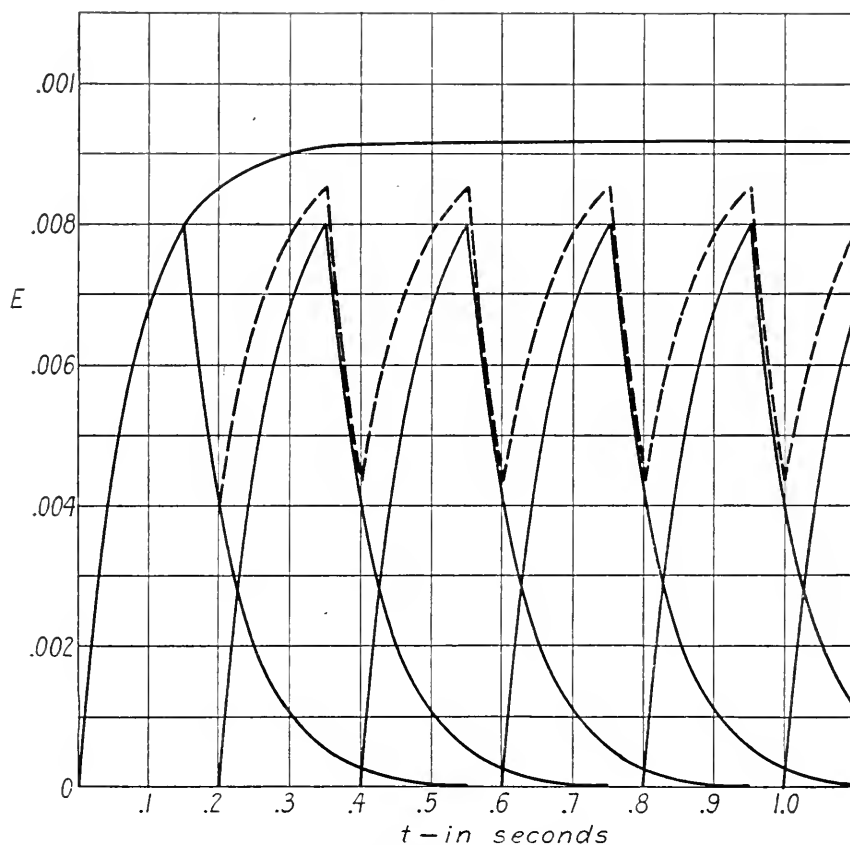
syllable is not far from .2 second. The accuracy of this value will not affect our conclusions appreciably. We shall assume that for each syllable emission proceeds at a constant rate and that successive syllables are separated by intervals of .05 second during which no emission occurs. In Fig. 3 are shown the intensity-

<sup>3</sup>"Analysis of the Energy Distribution in Speech," I. B. Crandall and D. MacKenzie, *Phys. Rev.*, March, 1922, 19, p. 221.



growth and decay curves of a number of successive syllables, computed for a room of small absorbing power. The total intensity-time curve for the room is obtained by adding the intensity-time curves of all the syllables. This is shown as the dash line curve in the figure. It shows a piling up of sound and relatively small intensity changes between syllables. This is sufficient explanation for the impossibility of hearing comfortably in the room. The

FIG. 4.



Growth and decay of sound intensity for syllable emission in a room of proper absorbing power.

construction of the figure shows that improvement will result from a slower pace by the speaker, a fact which speakers would do well to keep in mind. The figure further indicates that although the slower pace may strike the speaker as being disjointed, the audience will receive no such impression. The upper curve in the figure shows the intensity which would obtain for perfectly continuous emission at the same rate.

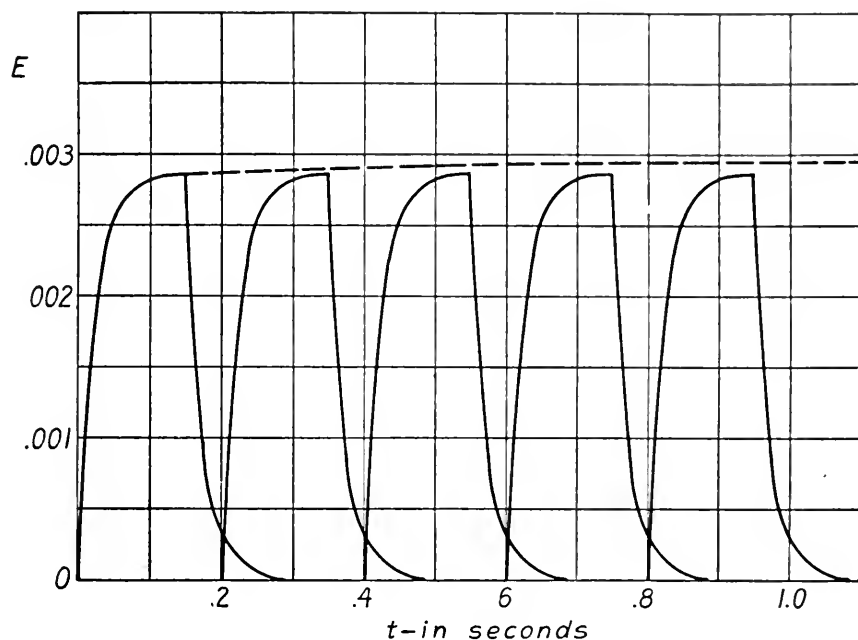
Fig. 4 applies to a room of the same size as Fig. 3 in which, however, the interior finish has been so chosen as to provide satis-



factory acoustical conditions. The standards on which this choice is based will be discussed presently. In this room there is little of the piling up of sound energy and the intensity falls off considerably between syllables. It is rather obvious why this room should be more satisfactory than that to which Fig. 3 applies.

We may go several steps further and make the wall surfaces as absorbing as it is possible to do. The room to which Fig. 5

FIG. 5.



Growth and decay of sound intensity for syllable emission in a room of too great absorbing power.

applies is of this kind. It has the same volume as the rooms to which Figs. 3 and 4 apply. In this case the intensity for each syllable practically reaches the saturation value for continuous emission at the same rate. Very little sound intensity of a syllable remains when the succeeding syllable begins. The summation curve differs so little from the component curves that it has not been drawn.

The question is, "Why are the conditions of Fig. 5 not even better than those depicted in Fig. 4?" Anyone who has been in a felt-padded room knows that they are not. The answer is probably two-fold. First, the maximum intensity of speech in such a room is so very much below that obtaining in our usual surroundings that this circumstance impresses the observer as being



unnatural. The second point is that in our everyday surroundings we have become so accustomed to a certain amount of syllable overlapping that a departure from these conditions, even in the direction which *a priori* would seem to be more satisfactory, is regarded as unsatisfactory.

We see, therefore, that a room may have too little as well as too much reverberation. Too much reverberation results in confusion and too little is judged unsatisfactory for reasons not so evident. In the latter case the sound is described as being dead, lifeless. This at once raises the question whether general agreement can be had as to what constitutes a satisfactory degree of reverberation. This point was investigated experimentally by Professor Sabine,<sup>4</sup> who altered the absorbing powers of a number of rooms by the progressive introduction and removal of absorbing materials until a condition was reached at which the persons present considered a rendition of piano music to sound most satisfactory. These experiments were made most carefully to exclude all possibility of bias and the results revealed a remarkable uniformity of judgment.

Having recognized that there is a most satisfactory degree of reverberation and that substantial agreement can be had as to when it exists, we need to consider how we may determine to what extent the reverberation in a room which has been judged unsatisfactory departs from best conditions. If we had a sound intensity decay curve for a satisfactory room our problem of providing the best reverberation in all rooms would be simply that of bringing the intensity decay in each room into conformity with this optimum curve. But the decay curve, being logarithmic, is completely defined if we state in what interval of the variable  $t$  the quantity  $E$  decreases from the value  $E_{\max}$  to  $1/\epsilon$  times that value. In conformity with the practice in similar physical problems this time interval may appropriately be called the relaxation time of the room and is given by

$$T_{\epsilon} = \frac{4V}{vaS} \quad (11)$$

This is the time in which the sound in a room decays from the saturation value to  $1/\epsilon$  times that value. The magnitude of this quantity  $T_{\epsilon}$ , even for very large rooms, is a fraction of a

---

<sup>4</sup> Wallace C. Sabine, "Collected Papers on Acoustics," p. 71.



second. The impracticability of measuring or estimating sound intensity decay over so short a time interval makes the relaxation time thus defined unsuited for practical use. It would seem feasible to devise apparatus for recording the decay of sound intensity in a room with respect to time and to determine the value of  $T_{\epsilon}$  from the graphical record. This was attempted by Professor Sabine and others, and it was found that the actual sound decay curve, instead of being nicely logarithmic, is in general a curve with many maxima and minima from which it is difficult to sift out the logarithmic component with sufficient precision. The complication of the curve is of course due to the interferences which we decided to ignore.

It is a remarkable fact that although the interferences close the avenue of approach just discussed, Professor Sabine succeeded in devising a workable procedure in spite of them. This he did by using as his starting point the minimum quantity of sound energy that is audible and by using 1,000,000 times this minimum quantity as the saturation energy density (sound intensity) at which the intensity decay begins. The time in which the decay from one value to the other takes place he called the reverberation time. This is expressed in terms of equation (10) as follows:

$$10^{-6} = \epsilon^{-\frac{vaS}{4V}T} \quad (12)$$

where  $T$  = the reverberation time. The solution of this equation is<sup>5</sup>

$$T = \left( \frac{4}{v} \log_e 10^6 \right) \frac{V}{aS} = .160 \frac{V}{aS} \quad (13)$$

which is the reverberation time equation of Professor Sabine.

The decay of sound intensity in a room is, therefore, characterized by a measurable reverberation time. Since there is a best rate of intensity decay there is a best reverberation time. The amount of departure of the reverberation time from this best value is a measure of the departure of the reverberation from its most satisfactory degree.

---

<sup>5</sup> Since the velocity of sound enters into the constant of this equation, the constant varies with temperature. The value in equation (13) is based on a temperature of 20° C. or 68° F. If foot units are more convenient the reverberation time equation in terms of cubic feet volume and square feet area units is

$$T = .048 \frac{V}{aS}$$



As presented here, the value of the constant in the reverberation time equation (13) results from the mathematical analysis of the reverberation problem. On the other hand, Professor Sabine derived the constant from actual reverberation experiments. The agreement of the theoretical and experimental values is remarkably good.

We can readily see by inspection of equation (13) how the reverberation time of a room may be computed in advance of construction.

We need to know only its volume and its absorbing power. The whole thing, therefore, practically dwindles down to computing the absorbing power of the room. In doing so we group all areas having the same absorption coefficient and multiply each such area by the absorption coefficient peculiar to it. The sum of the resulting products for all the component surfaces of the room is the absorbing power. Symbolically

$$\text{Absorbing power} = a_1S_1 + a_2S_2 + \cdots + a_nS_n = \sum_{i=1}^{i=n} a_iS_i \quad (14)$$

The mean absorption coefficient used in the general formulas (7) to (9) is defined by the relation

$$a = \frac{\sum_{i=1}^{i=n} a_iS_i}{\sum_{i=1}^{i=n} S_i} \quad (15)$$

After the absorbing power has been found by use of equation (14), substitution in (13) will yield the corresponding reverberation time.

Equation (14) is implicitly based on the assumption that the arrangement of the absorbing surfaces has no effect upon the magnitude of the absorbing power of the room and is valid only to the extent to which this assumption is in accord with the facts. In most cases encountered by the architect this accord is sufficiently good for practical purposes.

It is true, in general, that for satisfactory results the reverberation time should be a little greater than one second if the room is to be used for speaking, and a little less than two seconds if the room is to be used primarily for music. If mixed uses are contemplated a compromise must, of course, be made. If the com-



puted reverberation time departs from the optimum value, equation (13) may be used to determine how much change must be made in the absorbing power of the room to assure optimum conditions. If the reverberation time is too small some surface area must be made less absorbing by using material of smaller absorption coefficients. This can practically always be accomplished in a variety of ways and one can usually find at least one which is entirely compatible with other requirements. If, as is more usual, the reverberation time is too large, more absorbing materials must be provided in the construction. The quantity of absorbing power to be added usually gives a clue as to the best manner of securing it. In some cases none of the usual building materials will be adequate and material will have to be used for the sake of its sound-absorbing qualities alone. The most highly absorbing material known is hair felt, but it adds neither finish nor strength to the room in which it is used. The situation would be ideal if sound-absorbing materials were good finishing materials as well, so that interior finish and proper reverberation could be secured by the use of a single material. Development of building materials of this type is a problem of the future.<sup>6</sup> In order to have real practical utility such materials must be readily available and not prohibitively expensive.

It must not be forgotten that the people present in an auditorium contribute, usually appreciably and often preponderatingly, to the absorbing power of a room. It is therefore necessary when computing the reverberation time to be expected to include in the absorbing power of the room an item for the average estimated audience. The absorbing power per individual in an audience is given by Sabine<sup>7</sup> as .44 square metre unit.<sup>8</sup> For an estimated average audience of  $n$  people an absorbing power of .44  $n$  must be added to the other component absorbing powers in computing the total for the room. If the audience is smaller than the estimated average the reverberation time will exceed the optimum

---

<sup>6</sup> An interesting example of a material of this type is the Guastavino tile.

<sup>7</sup> Sabine, "Collected Papers on Acoustics," p. 58.

<sup>8</sup> It must be remembered that this quantity .44 per individual is an *absorbing power* with the dimensions of an area. An average person absorbs as much sound energy as .44 square metre of a hypothetical totally absorbing substance (open window). If English units are used this number must be multiplied by 10.8, the number of square feet in a square metre.



value. An auditorium which is satisfactory with a capacity audience is, therefore, likely to be very unsatisfactory when most of the seats are unoccupied. On the other hand, an auditorium which would be satisfactory with 5 per cent. of a capacity audience would be dead with a full house. This difficulty can be minimized by designing the room acoustically for a capacity audience and by curtaining off unused galleries and alcoves for smaller audiences, thus simultaneously diminishing the volume and introducing highly absorbing surfaces.

It is quite impossible to discuss within the limits of this paper more than the merest fundamentals of the reverberation computations which can profitably be made in the course of design. We have thus far ignored the fact that the absorption coefficient of materials varies with the pitch of the sound and with its intensity. This is a difficulty but also a happy circumstance. Those who would provide reasonably good acoustics can usually overlook these facts. Those who would provide a masterpiece may not ignore them.

The procedure for correcting rooms which present unsatisfactory reverberation conditions is also indicated by the reverberation time equation (13). The reverberation time is determined experimentally in the vacant room and the volume is determined by measurement or from the plans. By substituting these values in the equation we obtain the magnitude of the absorbing power of the vacant room. From equation (13) we may also determine how much the absorbing power of the room should be in order to provide an optimum reverberation time. The difference of these two values is the corrective change of absorbing power which must be made. In most cases the absorbing power must be increased. In this case  $x$ ,  $y$ , and  $z$  square feet of materials  $a$ ,  $b$ , and  $c$  will give the desired amount of additional absorbing power. But there is not enough wall space available to apply  $x$  square feet of material  $a$ , and some surfaces are not suitable for treatment with material  $b$ . A combination of  $u$  square feet of material  $a$  and  $v$  square feet of material  $b$  gives the desired absorbing power and can be applied without harming the appearance of the room.

The whole procedure is relatively simple with the exception of the measurement of the reverberation time. It is not merely a matter of making a loud sound and measuring the duration of its audibility with a stop-watch. To be precise we must be certain



that the sound intensity in the room when the sound source is stopped off is 1,000,000 times the least audible intensity. If the initial sound were only 100,000 times the minimum audibility value the measured reverberation time would be too small by  $16\frac{2}{3}$  per cent. If we know the value of the initial intensity in terms of the minimum audibility intensity we can of course reduce the observed reverberation time to standard conditions. But the measurement of the initial intensity is quite difficult. The available devices for measuring sound intensity cannot be used effectively because the sound intensity at each point in the room is constantly changing due to the shifting interference pattern, and if the sound field were relatively stationary it would be necessary to make measurements at a large number of positions in order that the result might represent the average intensity throughout the room. Professor Sabine solved the problem of measuring the initial intensity elegantly by suitable reverberation time measurements.<sup>9</sup>

It is obvious that the correction of reverberation is not as simple as its avoidance. In most corrective problems coming within my personal experience the rooms investigated had only one-eighth to one-half of the optimum absorbing power. In such cases a value of the reverberation time which can be relied upon to be correct to 5, or even 10, per cent. may be of considerable value. We saw in equation (8) (p. 802) that the maximum intensity in the room is given by  $4A/\pi aS$ . The initial intensity in a room may, therefore, be computed from the rate of emission of the source and the absorbing power of the room. If we have a source of sound the rate of emission of which can be reliably reproduced, we can estimate the maximum intensity in a room to the same accuracy that we can estimate its absorbing power. If our estimate of the absorbing power ranges from five times too large to five times too small, the consequent error in the reverberation time will be less than 12 per cent. The reason for this is obvious from equation (13). With a little experience one can easily approximate the absorbing power well within these limits and relatively good reverberation times may be obtained.

The foregoing discussion is confined to only one phase of the acoustical problem confronting the architect. Reverberation is the most important of these problems and the one most frequently

---

<sup>9</sup> Sabine, "Collected Papers on Acoustics," pp. 34-40.



encountered. The focussing of sound by curved walls making the sound intensity abnormally large in some places and small in others is another difficulty to be considered. Loud echoes may result from this cause. Then there are resonances and interferences which defeat the aim to secure a uniform distribution of sound intensity.

We shall have to rest content, however, with our consideration of reverberation and I trust that its discussion here presented may be of some assistance to those interested in securing satisfactory hearing conditions in rooms.

---

**Reciprocal Diffraction Relations between Circular and Elliptical Plates.** JOHN COULSON and G. G. BECKNELL. (*Phys. Rev.*, Dec., 1922.)—"Early in the nineteenth century Poisson predicted that if the Huyghens-Fresnel theory were correct, the light intensity behind a small opaque disc illuminated by a point source should be about the same as though the disc were removed. Arago verified this experimentally, using a disc about 2 mm. in diameter. In a later paper Arago states that the same phenomenon was discovered by Delisle in 1715." In this series of experiments performed at the University of Pittsburgh a pinhole .3 mm. in diameter illuminated by an arc light served as the source of light, which fell upon a circular disc 2 metres distant. Five metres beyond the disc was placed the photographic plate on which the light impression was registered. This was merely a tiny circle of light when the disc was held perpendicular to the light from the pinhole. When the disc was turned about an axis in its plane the Arago spot developed into a figure with four cusps which expanded outward as the disc was turned further. The same figure was obtained by substituting for the turned disc an elliptical disc placed at right angles to the light, its minor axis equal to the diameter of the circular disc and its major axis determined according to the angle of rotation. "Careful measurements of the photographs prove that in each case the diffraction pattern is the evolute of the geometrical shadow. The effect is as though each element of the edge of the shadow contributed a spot along its normal, the result being a caustic curve of refraction." This consideration is pursued in a second paper in the same number of the *Review*. Further photographs were made with longer distances from the pinhole to the plate. In one case this distance was as much as 33 metres. Much information as to the structure of the diffraction figures was obtained. Very clear color effects were noted. This general conclusion is reached: "Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object." G. F. S.



# THE SOLUTION OF DIFFERENTIAL EQUATIONS BY A METHOD SIMILAR TO HEAVISIDE'S.\*

BY

J. J. SMITH, M.A., M.S.

Union College, Schenectady, New York.

## SYNOPSIS.

*Systems of a Finite Number of Degrees of Freedom.*—The classical method of solution of linear differential equations, together with the solution by means of Heaviside's expansion theorem, is briefly discussed. A new method, which is called for convenience "the method of elimination," of solving a linear differential equation of the second order with constant coefficients and a constant impressed force which is applied at the instant  $t = 0$  is then given, and this is immediately extended to equations of the  $n$ th order. It is shown how the solution may be obtained when the equations have multiple roots, even though the method seems at first sight to break down. The application to the case of a force which can be represented by a Fourier series, and which is applied at the instant  $t = 0$  follows. For the solution of this problem certain operators are derived by means of the method of successive approximations in integral equations.

*Systems of an Infinite Number of Degrees of Freedom.*—On solving certain of the partial differential equations in the flow of heat and electricity by the method of successive approximations in integral equations, a linear differential equation of an infinite order is obtained. By applying the "method of elimination" to this equation a solution is obtained which coincides with the one obtained by the classical theory. The points of resemblance of this solution to Heaviside's method of solution are noted and an operational notation very similar to his is adopted. An example is given which involves a partial differential equation of three independent variables. The possibility of the solution of potential problems is illustrated by some examples and the difficulties encountered are pointed out. A method of deriving definite integrals, by means of operators, is given, and a suggestion is made of the generalization of a result due to Fredholm.

---

\* Communicated by E. J. Berg, D.Sc., Professor of Electrical Engineering.



## INTRODUCTION.

The solution of certain problems in physics and engineering often resolves itself into the question of solving a system of linear differential equations with constant coefficients. Ordinarily the general solution of these equations is found and the constants of integration determined so as to fit the initial conditions. For example, it is known that the solution of the equation

$$\frac{d^n y}{dt^n} + a_1 \frac{d^{n-1} y}{dt^{n-1}} + a_2 \frac{d^{n-2} y}{dt^{n-2}} + \cdots + a_{n-1} \frac{dy}{dt} + a_n y = E \quad (1)$$

is given by

$$y = \frac{E}{a_n} + A_1 e^{m_1 t} + A_2 e^{m_2 t} + \cdots + A_n e^{m_n t} \quad (2)$$

where  $m_1, m_2, \dots, m_n$  are the roots of the equation

$$m^n + a_1 m^{n-1} + a_2 m^{n-2} + \cdots + a_{n-1} m + a_n = 0 \quad (3)$$

The method of solution of this problem seems to have been to make a guess at the form of the general solution and then to show that it satisfies the differential equation.

Heaviside introduced the symbol  $p$  for  $\frac{d}{dt}$ , subject to the condition that  $p^2$  symbolized  $\frac{d^2}{dt^2}$  and in general  $p^n$  symbolized  $\frac{d^n}{dt^n}$ , and he further assumed that  $p$  conformed (under certain restrictions) to the laws of ordinary algebra. Making this substitution equation (1) becomes

$$p^n y + a_1 p^{n-1} y + \cdots + a_{n-1} p y + a_n y = E \quad (4)$$

Hence

$$y = \frac{E}{p^n + a_1 p^{n-1} + \cdots + a_{n-1} p + a_n} \quad (5)$$

Splitting the expression on the right-hand side of this equation into partial fractions, it becomes,

$$y = \frac{c_1 E}{p - \alpha} + \frac{c_2 E}{p - \beta} + \cdots + \frac{c_n E}{p - \nu} \quad (6)$$

where  $\alpha, \beta, \dots, \nu$  are the roots of the polynomial in  $p$  in the



denominator of (5), and  $c_1, c_2, \dots, c_n$  are constants which can easily be determined.

He then expanded each of these fractions in powers of  $\frac{1}{p}$ , and very ingeniously got a value for  $\frac{1}{p-\alpha} = \frac{1}{-\alpha} (1 - e^{\alpha t})$  subject to the conditions that (a) the initial displacement of every coördinate shall be zero; (b) the initial velocity of every coördinate shall be zero. These two assumptions will be called Heaviside's terminal conditions.

From this he develops his "expansion theorem" <sup>1</sup> which is that, if  $\frac{d}{dt}$  is replaced by  $p$  in the original equations and when these are solved in the usual manner, the symbolic equation

$$y = \frac{EY(p)}{Z(p)} \quad (7)$$

is obtained where  $Y(p)$  and  $Z(p)$  denote some functions of  $p$ , then the actual value of  $y$  under the conditions (a) and (b) is

$$y = E \left[ \frac{Y(0)}{Z(0)} + \sum \frac{Y(p_m) e^{p_m t}}{p_m \left( \frac{dZ}{dp} \right)_{p=p_m}} \right] \quad (8)$$

where the summation is taken over the roots of  $Z(p)$ .

Heaviside's proof of this theorem, which is given in a footnote in his "Electrical Papers" (vol. 2, p. 373), has not seemed rigorous to mathematicians and in recent years other methods of proof have been evolved. Bromwich <sup>2</sup> gives a demonstration which depends upon the use of a certain contour integral, and Carson <sup>3</sup> solves it by going back to a consideration of the original differential equation.

The following method seems to have some advantage over both of these proofs, as it actually shows the mechanism through which the result is derived, and it allows the use of theorems concerning the convergence of infinite products in connection with the solution of a linear equation of an infinite order.

<sup>1</sup> Heaviside, "Electromagnetic Theory," vol. 2, p. 127 *et seq.* Also two papers by Cohen in recent numbers of this JOURNAL.

<sup>2</sup> Bromwich, *Proc. Lond. Mat. Soc.*, [Ser. 2] 1916, 15, p. 401.

<sup>3</sup> Carson, *Phys. Rev.*, N. S., 1917, 10, No. 3, p. 217.



## SOLUTION OF LINEAR DIFFERENTIAL EQUATION OF SECOND ORDER.

Take as an example the simple equation

$$\frac{d^2y}{dt^2} + b \frac{dy}{dt} + c = E \quad (9)$$

where  $b$ ,  $c$ , and  $E$  are constants. This can be written

$$\left(\frac{d}{dt} - \alpha\right) \left(\frac{d}{dt} - \beta\right) y = E \quad (10)$$

where  $\alpha$  and  $\beta$  are the roots of the equation

$$m^2 + bm + c = 0.$$

Equation (10) is the usual operational way of writing (9), which will be found in most text-books on differential equations, and it is easily shown that the order of the operational factors may be reversed and the equation written

$$\left(\frac{d}{dt} - \beta\right) \left(\frac{d}{dt} - \alpha\right) y = E. \quad (10a)$$

Equation (10) can be solved by finding a function  $u$  such that

$$\left(\frac{d}{dt} - \alpha\right) u = E. \quad (11)$$

The solution of (11) subject to the condition  $u = 0$  when  $t = 0$  is

$$u = \frac{E}{-\alpha} (1 - e^{\alpha t}) \quad (12)$$

Substituting this value of  $u$  in the left-hand side of equation (11) and equating to the left-hand side of (10) since both are equal to  $E$ , then

$$\left(\frac{d}{dt} - \alpha\right) \left[\frac{E}{-\alpha} (1 - e^{\alpha t})\right] = \left(\frac{d}{dt} - \alpha\right) \left(\frac{d}{dt} - \beta\right) y \quad (13)$$

which gives <sup>4</sup>

$$\frac{E}{-\alpha} (1 - e^{\alpha t}) = \left(\frac{d}{dt} - \beta\right) y \quad (14)$$

<sup>4</sup> Actually if

$$\left(\frac{d}{dt} - \alpha\right) A = \left(\frac{d}{dt} - \alpha\right) B$$

then

$$A - B = Ce^{\alpha t}$$

but for a solution subject to Heaviside's conditions  $C = 0$ .



Similarly find a function  $v$  such that subject to the condition  $v = 0$  when  $t = 0$

$$\left(\frac{d}{dt} - \beta\right)v = E \quad (15)$$

then

$$v = \frac{E}{-\beta} (1 - e^{\beta t}) \quad (16)$$

and proceeding in the same manner as above with (10a) instead of (10)

$$\frac{E}{-\beta} (1 - e^{\beta t}) = \left(\frac{d}{dt} - \alpha\right)y \quad (17)$$

subtracting (17) from (14) the  $\frac{dy}{dt}$  term disappears and the result is

$$y = E \left[ \frac{1}{\alpha\beta} + \frac{e^{\alpha t}}{\alpha(\alpha - \beta)} + \frac{e^{\beta t}}{\beta(\beta - \alpha)} \right]. \quad (18)$$

This is exactly the result which is obtained by applying Heaviside's expansion theorem. The important point to notice is that this equation of the second order is solved by means of the solution of two linear equations of the first order, and then by the elimination of  $\frac{dy}{dt}$  from the resulting two equations.

#### SOLUTION OF SIMULTANEOUS EQUATIONS OF $n$ th ORDER.

The method of dealing with the general equation of the  $n$ th order is now apparent. If the above process is applied to each of the  $n$  factors  $\frac{d}{dt} - \alpha_p$  where  $p = 1, 2, 3, \dots, n$ , the result is  $n$  equations in which the variables may be considered as  $\frac{d^{n-1}y}{dt^{n-1}}$ ,  $\frac{d^{n-2}y}{dt^{n-2}}$ ,  $\dots$ ,  $\frac{dy}{dt}$ ,  $y$ , and provided the determinant of this system does not vanish, it is possible to determine  $y$  by elimination. If the equations are solved subject to Heaviside's terminal conditions his expansion theorem is obtained. If they are solved subject to arbitrary initial conditions, the  $n$  resulting constants can be determined so as to satisfy these conditions. For example (12)



is the solution of (11) only if  $u = 0$  when  $t = 0$ . In general (12) could be written,

$$u = \frac{E}{-\alpha} \left( 1 - C_1 e^{\alpha t} \right) \quad (12a)$$

Similarly (16) could be written

$$v = \frac{E}{-\beta} \left( 1 - C_2 e^{\beta t} \right) \quad (16a)$$

and by elimination

$$y = E \left[ \frac{1}{\alpha\beta} + \frac{C_1 e^{\alpha t}}{\alpha(\alpha - \beta)} + \frac{C_2 e^{\beta t}}{\beta(\beta - \alpha)} \right] \quad (18a)$$

where  $C_1$  and  $C_2$  are to be determined from the initial conditions. In the following the solution will be worked out subject to Heaviside's conditions, and it is evident the more general solution for an arbitrary initial state can be derived by multiplying each of the exponential terms in the result by arbitrary constants whose values are determined later in the usual way. The constant term, which corresponds to the permanent condition, is, however, independent of these arbitrary constants, as might be expected since the permanent condition does not depend upon the transient.

Let the system of linear differential equations be characterized by the following forms,

$$\begin{aligned} a_{11}y_1 + a_{12}y_2 + \dots + a_{1n}y_n &= F_1 \\ a_{21}y_1 + a_{22}y_2 + \dots + a_{2n}y_n &= F_2 \\ \dots & \\ \dots & \\ a_{n1}y_1 + a_{n2}y_2 + \dots + a_{nn}y_n &= F_n \end{aligned} \quad (19)$$

the general coefficient  $a_{jk}$  being of the form

$$a_{jk} = \alpha_{jk} \frac{d^n}{dt^n} + \beta_{jk} \frac{d^{m-1}}{dt^{m-1}} + \dots + \mu_{jk}$$

where  $\alpha_{jk}$ ,  $\beta_{jk}$ , . . .  $\mu_{jk}$  are constants.

The impressed forces  $F_1$ ,  $F_2$ , . . .  $F_n$  which begin to act at the time  $t = 0$  will be assumed to be constants. It is most convenient to solve these equations for each impressed force one at a time, *i.e.*, assume first that  $F_1$  acts and all the others are zero, then let  $F_2$  act and all the others be zero, continuing this until the effect of each one of the forces has been found. The solution when all the forces act together is got by summing up the separate solutions.



The differential equation obtained for  $y_k$  from (19) when the force  $F_r$  is assumed to act alone is

$$Dy_k = M_{rk}F_r \tag{20}$$

where  $D$  is the value of the determinant,

$$\begin{vmatrix} a_{11} & a_{12} & \cdots & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & \cdots & a_{2n} \\ \cdots & \cdots & & & \cdots \\ \cdots & \cdots & & & \cdots \\ \cdots & \cdots & & & \cdots \\ a_{n1} & a_{n2} & \cdots & \cdots & a_{nn} \end{vmatrix} \tag{20a}$$

and  $M_{rk}$  is the minor of the  $r$ th row and  $k$ th column.

Writing (20) out in full it becomes

$$\begin{aligned} \left(\frac{d}{dt} - \alpha\right) \left(\frac{d}{dt} - \beta\right) \cdots \left(\frac{d}{dt} - \nu\right) y_k &= \left(\frac{d}{dt} - a_r\right) \left(\frac{d}{dt} - b_r\right) \\ &\cdots \left(\frac{d}{dt} - n_r\right) F_r \end{aligned} \tag{21}$$

where  $\alpha, \beta, \dots \nu$  are the roots of  $D$  regarded as a function of  $\frac{d}{dt}$  and  $a_r, b_r, \dots n_r$  are the roots of  $M_{rk}$ .

Determine  $\nu$  functions  $x_r^{(\alpha)}, x_r^{(\beta)} \cdots x_r^{(\nu)}$  such that subject to Heaviside's conditions,

$$\begin{aligned} \left(\frac{d}{dt} - \alpha\right) x_r^{(\alpha)} &= F_r \\ \left(\frac{d}{dt} - \beta\right) x_r^{(\beta)} &= F_r \\ \cdots &\cdots \\ \cdots &\cdots \\ \left(\frac{d}{dt} - \nu\right) x_r^{(\nu)} &= F_r. \end{aligned} \tag{22}$$

Then

$$\begin{aligned} x_r^{(\alpha)} &= \frac{F_r}{-\alpha} \left(1 - e^{\alpha t}\right) \\ x_r^{(\beta)} &= \frac{F_r}{-\beta} \left(1 - e^{\beta t}\right) \\ \cdots &\cdots \\ \cdots &\cdots \\ x_r^{(\nu)} &= \frac{F_r}{-\nu} \left(1 - e^{\nu t}\right) \end{aligned} \tag{23}$$

Putting these values of  $x_r^{(\alpha)}, x_r^{(\beta)} \cdots x_r^{(\nu)}$  in equations (22), then substituting the  $\nu$  values of  $F_r$  so obtained in (21) and can-







Subtracting the second equation in (25) from the first and dividing by  $(\beta - \alpha)$ .

$$\begin{aligned} & \left( \frac{d}{dt} - \gamma \right) \left( \frac{d}{dt} - \delta \right) \cdots \left( \frac{d}{dt} - \nu \right) y_k \\ &= F_r \left[ \frac{(-a_r)(-b_r) \cdots (-n_r)}{(-\alpha)(-\beta)} + \frac{(\alpha - a_r)(\alpha - b_r) \cdots (\alpha - n_r)e^{\alpha t}}{\alpha(\alpha - \beta)} \right. \\ & \quad \left. + \frac{(\beta - a_r)(\beta - b_r) \cdots (\beta - n_r)e^{\beta t}}{\beta(\beta - \alpha)} \right] \end{aligned} \quad (26)$$

Subtracting the third equation from the first and rearranging

$$\begin{aligned} & \left( \frac{d}{dt} - \beta \right) \left( \frac{d}{dt} - \delta \right) \cdots \left( \frac{d}{dt} - \nu \right) y_k \\ &= F_r \left[ \frac{(-a_r)(-b_r) \cdots (-n_r)}{(-\alpha)(-\gamma)} + \frac{(\alpha - a_r)(\alpha - b_r) \cdots (\alpha - n_r)e^{\alpha t}}{\alpha(\alpha - \gamma)} \right. \\ & \quad \left. + \frac{(\gamma - \alpha_r)(\gamma - b_r) \cdots (\gamma - n_r)e^{\gamma t}}{\gamma(\gamma - \alpha)} \right] \end{aligned} \quad (27)$$

By similarly subtracting the first and fourth, the first and fifth, etc., equations in (25)  $(\nu - 1)$  equations are derived.

Now subtract (27) from (26) and get after a slight simplification

$$\begin{aligned} & \left( \frac{d}{dt} - \delta \right) \left( \frac{d}{dt} - \eta \right) \cdots \left( \frac{d}{dt} - \nu \right) y_k \\ &= F_r \left[ \frac{(-a_r)(-b_r) \cdots (-n_r)}{(-\alpha)(-\beta)(-\gamma)} + \frac{(\alpha - a_r)(\alpha - b_r) \cdots (\alpha - n_r)e^{\alpha t}}{\alpha(\alpha - \beta)(\alpha - \gamma)} \right. \\ & \quad \left. + \frac{(\beta - a_r)(\beta - b_r) \cdots (\beta - n_r)e^{\beta t}}{\beta(\beta - \alpha)(\beta - \gamma)} + \frac{(\gamma - a_r)(\gamma - b_r) \cdots (\gamma - n_r)e^{\gamma t}}{\gamma(\gamma - \alpha)(\gamma - \beta)} \right] \end{aligned} \quad (28)$$

$(\nu - 2)$  equations similar to (28) can be obtained. By continuing this process, which will be called the "method of elimination," the value of  $y_k$  is obtained in the standard form of Heaviside's expansion theorem. The general case may be easily proved by induction.

It might have been suggested perhaps that in equation (21) since  $F_r$  is a constant, the right-hand side could have been written  $(-a_r)(-b_r) \cdots (-n_r)F_r$ , and apparently if this had been done a different final expression for Heaviside's expansion theorem would have been obtained, *i.e.*, in (28) each of the numerators of the exponential terms would have been  $(-a_r)(-b_r) \cdots (-n_r)$  instead of, for example,  $(\alpha - a_r)(\alpha - b_r) \cdots (\alpha - n_r)$ . This is due to the fact that  $F_r$  is a discontinuous function. It is zero when  $t < 0$  and equal to a constant value when  $t > 0$ . The



method adopted above of performing the differential operations in (24), where the discontinuous function  $F_r$  has been replaced by the continuous functions  $\frac{F_r}{-\alpha} (1 - e^{\alpha t})$ , etc., avoids this difficulty.

#### CASE WHERE $D$ HAS EQUAL ROOTS.

The method fails when  $D$ , regarded as a function of  $\frac{d}{dt}$ , has equal roots. Let  $\alpha$  be a root of the  $n$ th order. Assume that these roots are not all equal but are  $(\alpha + \varepsilon_1)$ ,  $(\alpha + \varepsilon_2)$ , . . .  $(\alpha + \varepsilon_n)$  where  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n$  are small quantities which ultimately approach zero as a limit. Applying the method for the sake of brevity to the equation

$$\left(\frac{d}{dt} - \alpha\right)^n y = E \quad (29)$$

after these  $n$  equal roots have been replaced by the  $n$  unequal ones, the result is

$$\begin{aligned} y = & \frac{E}{(-\alpha - \varepsilon_1)(-\alpha - \varepsilon_2) \cdots (-\alpha - \varepsilon_n)} \\ & + \frac{Ee^{(\alpha + \varepsilon_1)t}}{(\alpha + \varepsilon_1)(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 - \varepsilon_3) \cdots (\varepsilon_1 - \varepsilon_n)} + \frac{Ee^{(\alpha + \varepsilon_2)t}}{(\alpha + \varepsilon_2)(\varepsilon_2 - \varepsilon_1) \cdots (\varepsilon_2 - \varepsilon_n)} \\ & + \cdots + \frac{Ee^{(\alpha + \varepsilon_n)t}}{(\alpha + \varepsilon_n)(\varepsilon_n - \varepsilon_1) \cdots (\varepsilon_n - \varepsilon_{n-1})} \end{aligned} \quad (30)$$

The limit of the first term is evidently  $\frac{E}{(-\alpha)^n}$ . The other terms may be rewritten

$$\begin{aligned} Ee^{\alpha t} \left[ \frac{1 + \varepsilon_1 t + \frac{\varepsilon_1^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_1)(\varepsilon_1 - \varepsilon_2) \cdots (\varepsilon_1 - \varepsilon_n)} + \frac{1 + \varepsilon_2 t + \frac{\varepsilon_2^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_2)(\varepsilon_2 - \varepsilon_1) \cdots (\varepsilon_2 - \varepsilon_n)} \right. \\ \left. + \cdots + \frac{1 + \varepsilon_n t + \frac{\varepsilon_n^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_n)(\varepsilon_n - \varepsilon_1) \cdots (\varepsilon_n - \varepsilon_{n-1})} \right] \end{aligned}$$

Picking out the coefficient of  $\frac{t^q}{q!}$  inside this square bracket when  $q < n$ , it is seen to be the expansion in partial fractions of

$$\frac{(-1)^{n-1} \alpha^q}{(\alpha + \varepsilon_1)(\alpha + \varepsilon_2) \cdots (\alpha + \varepsilon_n)}$$

and the limit of this expression when  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n \rightarrow 0$  is  $\frac{(-1)^{n-1}}{\alpha^{n-q}}$



When  $q \geq n$  the coefficient is the expansion in partial fractions of

$$R = \frac{(-1)^{n-1} \alpha^q}{(\alpha + \epsilon_1)(\alpha + \epsilon_2) \cdots (\alpha + \epsilon_n)} - (-1)^{n-1} \alpha^{q-n} - f(\alpha)$$

where  $f(\alpha)$  tends to zero, when  $\epsilon_1, \epsilon_2, \cdots \epsilon_n \rightarrow 0$ . Hence when  $\epsilon_1, \epsilon_2, \cdots \epsilon_n \rightarrow 0$ ,  $R$  itself tends to zero.

Thus the solution of (29) is

$$y = \frac{E}{(-\alpha)^n} + (-1)^{n-1} \frac{Ee^{\alpha t}}{\alpha^n} \left( 1 + \alpha t + \frac{\alpha^2 t^2}{2!} + \cdots + \frac{\alpha^{n-1} t^{n-1}}{(n-1)!} \right) \tag{31}$$

This solution can be easily generalized to the case where  $\alpha, \beta, \gamma, \dots \nu$  are multiple roots of orders  $m, n, p, \dots s$ , the multiple root  $\alpha$  of order  $m$  giving rise to the exponential term

$$\frac{(-1)^{m-1} Ee^{\alpha t}}{\alpha^m (\alpha - \beta)^n (\alpha - \gamma)^p \cdots (\alpha - \nu)^s} \left[ 1 + \alpha t + \frac{\alpha^2 t^2}{2!} + \cdots + \frac{\alpha^{m-1} t^{m-1}}{(m-1)!} \right]$$

with similar exponential terms for  $\beta, \gamma, \dots \nu$ . The constant term is

$$\frac{E}{(-\alpha)^m (-\beta)^n \cdots (-\nu)^s}$$

APPLIED FORCE NOT A CONSTANT.

When the applied force can be represented by a Fourier series, if the solution can be found for each harmonic acting alone, then the sum of the solutions for each separate harmonic is the solution for the given applied force. The problem therefore resolves itself into finding a solution when the impressed force varies as a sine wave. There are several ways of proceeding in this case. Carson<sup>5</sup> gives a special expansion theorem, for which reference may be made to his paper. This method will not be discussed here. Heaviside replaces the impressed force  $F \cos \omega t$  by the operator  $\frac{p^2}{p^2 + \omega^2} F$  and then applies his expansion theorem in the usual manner. The analogue of this method would be to notice that,

$$\left( 1 + \omega^2 \int_0^t \int_0^t dt dt \right) F \cos \omega t = F \tag{32}$$

<sup>5</sup> Carson, *Phys. Rev.*, N. S., 1917, 10, No. 3, p. 217.



Hence operating on both sides of (21) with  $\left(1 + \omega^2 \int_0^t \int_0^t dt dt\right)$  after having replaced  $F_r$  by  $F_r \cos \omega t$  and changing the order of operations

$$\begin{aligned} & \left(1 + \omega^2 \int_0^t \int_0^t dt dt\right) \left(\frac{d}{dt} - \alpha\right) \cdots \left(\frac{d}{dt} - \nu\right) y_k = \\ & \left(\frac{d}{dt} - a_r\right) \left(\frac{d}{dt} - b_r\right) \cdots \left(\frac{d}{dt} - n_r\right) F_r \end{aligned} \quad (33)$$

where  $F_r$  is now a constant as before. Differentiating this twice, it becomes

$$\begin{aligned} & \left(\frac{d^2}{dt^2} + \omega^2\right) \left(\frac{d}{dt} - \alpha\right) \left(\frac{d}{dt} - \beta\right) \cdots \left(\frac{d}{dt} - \nu\right) y_k = \\ & \frac{d^2}{dt^2} \left(\frac{d}{dt} - a_r\right) \left(\frac{d}{dt} - b_r\right) \cdots \left(\frac{d}{dt} - n_r\right) F_r \end{aligned} \quad (34)$$

the solution of which is readily found by the Heaviside expansion theorem.

Similar operators can be found which transform  $F \sin \omega t$ ,  $F e^{-\alpha t} \sin \omega t$ , etc., into  $F$  and the expansion theorem thus extended to these cases. The determination of suitable operators will be briefly discussed in the next section.

Another mode of solution which is suggested by the method of elimination outlined above is to solve equation (22) where  $F_r$  is replaced by  $F_r \sin \omega t$  or  $F_r \cos \omega t$ . This will give new values for  $x_r^{(\alpha)}$ ,  $x_r^{(\beta)}$ , . . .  $x_r^{(\nu)}$  in (23). Then substituting in (24) and using the method of elimination, the result is easily obtained. The final expression is not given here as it is rather cumbersome to write out in full.

#### SOLUTION OF INTEGRAL EQUATIONS BY SUCCESSIVE APPROXIMATIONS.

In order to apply the method outlined here to continuous systems, it will be necessary to use the method of successive approximations in the solution of integral equations.<sup>6</sup> To recall this method and at the same time derive some other results, a few examples will be taken.

Let

$$\left(\frac{d}{dt} - \alpha\right) y = E \quad (35)$$

Integrating from 0 to  $t$  and rearranging

$$y = y_0 + Et + \alpha \int_0^t y dt \quad (36)$$

---

<sup>6</sup> Whittaker and Watson, "Modern Analysis," 1915, 2nd ed., p. 215.



where  $y_0 = (y)_{t=0}$ . This is a linear equation of the second kind for  $y$ . The method of successive approximations is to substitute the value of  $y$  as given by the equation itself for  $y$  under the integral sign. Doing this and carrying out the integration on the first two terms, the equation becomes,

$$y = y_0 + y_0 \alpha t + Et + E\alpha \frac{t^2}{2!} + \alpha^2 \int_0^t \int_0^t y dt dt \quad (37)$$

Substituting again the value of  $y$  given by the equation under the integral sign and continuing the process, finally

$$y = y_0 e^{\alpha t} + \frac{E}{-\alpha} (1 - e^{\alpha t}) \quad (38)$$

If Heaviside's terminal conditions apply, then  $y_0 = 0$  and

$$y = \frac{E}{-\alpha} (1 - e^{\alpha t}) \quad (39)$$

In the case where  $y_0 = 0$ , equation (36) may be written

$$\left(1 - \alpha \int_0^t dt\right) y = Et \quad (40)$$

Differentiating this

$$\left(1 - \alpha \int_0^t dt\right) \frac{dy}{dt} = E \quad (41)$$

But from (39)

$$\frac{dy}{dt} = E e^{\alpha t}. \quad (42)$$

Hence

$$\left(1 - \alpha \int_0^t dt\right) E e^{\alpha t} = E \quad (43)$$

This equation shows that  $\left(1 - \alpha \int_0^t dt\right)$  is the operator which transforms  $E e^{\alpha t}$  into the constant value  $E$ .

In a similar way, starting with the equation

$$\frac{d^2 y}{dt^2} = -\omega^2 y \quad (44)$$

and integrating twice from 0 to  $t$

$$y = y_0 + y_1 t - \omega^2 \int_0^t \int_0^t y dt dt \quad (45)$$

where  $y_0$  and  $y_1$  are the values of  $y$  and  $\frac{dy}{dt}$ , respectively, when



$t = 0$ . Solving this integral equation by successive approximations

$$y = y_0 \cos \omega t + \frac{y_1}{\omega} \sin \omega t \quad (46)$$

If  $y_1 = 0$ , substituting the value  $y = y_0 \cos \omega t$  in (45), it can be written,

$$\left(1 + \omega^2 \int_0^t \int_0^t dt dt\right) y_0 \cos \omega t = y_0 \quad (47)$$

which is the operator already used in equation (32).

If  $y_0 = 0$ , then (45) can be written,

$$\left(1 + \omega^2 \int_0^t \int_0^t dt dt\right) \frac{y_1}{\omega} \sin \omega t = y_1 t \quad (48)$$

and on differentiating this

$$\frac{d}{dt} \left(1 + \omega^2 \int_0^t \int_0^t dt dt\right) \frac{y_1}{\omega} \sin \omega t = y_1 \quad (49)$$

Hence  $\left(\frac{1}{\omega} \frac{d}{dt} + \omega \int_0^t dt\right)$  is the operator which transforms  $y_1 \sin \omega t$  into the constant  $y_1$ .

Another result which will be required later in connection with problems on the cylinder is the solution of Bessel's equation of the  $n$ th order,

$$\frac{d^2 y}{dt^2} + \frac{1}{t} \frac{dy}{dt} + \left(q^2 - \frac{n^2}{t^2}\right) y = 0 \quad (50)$$

If an attempt is made to integrate this equation directly, difficulties are encountered, since on the first integration the value of  $\left(t \frac{dy}{dt}\right)$  when  $t = 0$  is zero, and on the second integration the value of  $y$  when  $t = 0$  is the constant term. Now since it is already known that  $(y)_{t=0}$  or  $J_n(qt)$  vanishes to the order  $t^n$  when  $t = 0$ , the integral equation, is really one of the first kind. The fact that  $(y)_{t=0} = 0$  will become evident due to occurrence of infinite terms if the method of successive approximations is applied. Removing the factor  $t^n$  by the substitution  $y = t^n z$  (50) becomes<sup>7</sup>

$$\frac{d^2 z}{dt^2} + \frac{2n+1}{t} \frac{dz}{dt} + q^2 z = 0 \quad (51)$$

which may be written in the form

$$\frac{1}{t^{2n+1}} \frac{d}{dt} \left( t^{2n+1} \frac{dz}{dt} \right) + q^2 z = 0 \quad (52)$$

Integrating twice from 0 to  $t$

$$z = z_0 - q^2 \int_0^t \frac{1}{t^{2n+1}} \int_0^t t^{2n+1} z dt dt \quad (53)$$

<sup>7</sup> Byerly, Fourier Series, p. 23.



where  $z_0$  is the value of  $z$  when  $t = 0$ , it being taken that on the first integration the value of  $t^{2n+1} \frac{dz}{dt}$  is zero when  $t = 0$ .

Equation (53) can be solved by successive approximations giving

$$z = z_0 \left[ 1 - \frac{q^2 t^2}{2(2n+2)} + \frac{q^4 t^4}{2 \cdot 4(2n+2)(2n+4)} - \text{etc.} \right] \quad (54)$$

and since  $y = t^n z$

$$y = z_0 t^n \left[ 1 - \frac{q^2 t^2}{2(2n+2)} + \frac{q^4 t^4}{2 \cdot 4(2n+2)(2n+4)} - \text{etc.} \right] \quad (55)$$

which is the standard form of  $J_n(qt)$  when  $z_0$  is suitably chosen. From (53) it is now evident that

$$\left( 1 + q^2 \int_0^t \frac{1}{t^{2n+1}} \int_0^t t^{2n+1} dt dt \right) \left( \frac{J_n(qt)}{t^n} \right) = 1 \quad (56)$$

giving an operator which transforms  $A \frac{J_n(qt)}{t^n}$  into the constant  $A$ .

A consideration of the lower limit in these integral equations brings out an interesting point. The complete specification of  $y$  at the time  $t$  would require that the lower limit of the integral, in (36) for instance, be taken as  $-\infty$ . Equations (37) and (38) are then equivalent to (36) only if  $E = 0$  when  $t < 0$ ; in other words, only if the force  $E$  is applied at the time  $t = 0$ . The same remarks apply to the other equations, and hence the operators derived above transform a force  $Ee^{\alpha t}$ ,  $E \sin \omega t$ , etc., which is applied at the moment  $t = 0$  into a constant force  $E$  applied at  $t = 0$ . Thus all these functions are discontinuous at  $t = 0$ , which is what is usually required in physical problems.

#### CONTINUOUS SYSTEMS.

Heaviside having derived his expansion theorem for an equation with a finite number of degrees of freedom, applies it to continuous systems and finds that it works. By its means he solved numerous partial differential equations, some of which have only been recently solved by other methods.<sup>8</sup> In the classical method a particular solution of the equation is first obtained and an infinite number of these added together so as to satisfy the initial conditions. In the recent book by Carslaw, "Introduction to the Mathematical Theory of the Conduction of Heat"

<sup>8</sup> Cf. Carslaw, "Conduction of Heat," 1921, p. 218, footnote; also p. 201.



(1922), some of the problems are worked out by four or five different methods, but in each of these solutions some initial assumption has to be made. It will now be shown how the application of the method of elimination enables the solution of a differential equation of an infinite order to be found and thus permits the solution of certain partial differential equations by a process which is purely mechanical. It will be found most convenient to take specific examples as illustrations. The first example is taken from Heaviside's work for the purpose of comparison. Most of the others will be found in the work by Carslaw referred to above, or in other works on heat. No attempt will be made here at a rigorous examination when infinite processes are involved.

#### TRANSMISSION LINE WITH RESISTANCE AND CAPACITY.

Consider a transmission line with resistance and capacity only. Let the line be short-circuited at the receiving end ( $x=0$ ) and let a constant voltage  $E$  be suddenly applied at the generating end ( $x=l$ ) when  $t=0$ .

The equations to be solved are

$$K \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \quad (57)$$

$$\left. \begin{aligned} v &= 0 \text{ when } x = 0 \\ v &= E \text{ when } x = l \quad (t > 0) \\ v &= 0 \text{ when } t = 0 \end{aligned} \right\} \quad (58)$$

where  $K = \frac{1}{CR}$ ,  $C$  and  $R$  being the capacity and resistance of the cable per unit length. Integrating (57)

$$\frac{\partial v}{\partial x} = C_1 + \frac{1}{K} \int_0^x \frac{\partial v}{\partial t} dx \quad (59)$$

where  $C_1 = \left( \frac{\partial v}{\partial x} \right)_{x=0}$  is a function of  $t$  only. On integrating again

$$v = C_1 x + \frac{1}{K} \int_0^x \int_0^x \frac{\partial v}{\partial t} dx dx \quad (60)$$

since  $(v)_{t=0} = 0$  from (58). Solving this as an integral equation for  $v$ , remembering  $C_1$  is a function of  $t$  alone, it becomes

$$v = \left( C_1 x + \frac{1}{K} \frac{\partial C_1}{\partial t} \frac{x^3}{3!} + \frac{1}{K^2} \frac{\partial^2 C_1}{\partial t^2} \frac{x^5}{5!} + \dots \right) \quad (61)$$



This is a linear differential equation of infinite order for  $C_1$ . From (58)  $v = E$  when  $x = l$ , hence writing  $C_1$  outside the bracket for the sake of convenience

$$E = \left( l + \frac{1}{K} \frac{l^3}{3!} \frac{\partial}{\partial t} + \frac{1}{K^2} \frac{l^5}{5!} \frac{\partial^2}{\partial t^2} + \dots \right) C_1 \quad (62)$$

But

$$\sinh p\theta = p\theta + \frac{p^3\theta^3}{3!} + \frac{p^5\theta^5}{5!} + \dots \quad (63)$$

and also

$$\sinh p\theta = p\theta \left( 1 + \frac{p^2\theta^2}{\pi^2} \right) \left( 1 + \frac{p^2\theta^2}{2^2\pi^2} \right) \dots \left( 1 + \frac{p^2\theta^2}{n^2\pi^2} \right) \dots \quad (64)$$

By comparing (63) and (64) it is evident (62) may be written in the factorial form

$$E = l \left( 1 + \frac{l^2}{K} \frac{\partial}{\partial t} \right) \left( 1 + \frac{l^2}{2^2\pi^2} \frac{\partial}{\partial t} \right) \dots \left( 1 + \frac{l^2}{n^2\pi^2} \frac{\partial}{\partial t} \right) \dots C_1 \quad (65)$$

It may be emphasized here that the transition from (62) to (65) is simply a question of identifying the coefficients  $\frac{1}{3!}$ ,  $\frac{1}{5!}$ , etc., in (62) with the sums of the various infinite series of constants obtained if (65) were multiplied out. This is most easily done by comparison with (63) and (64).

To solve (65) for  $C_1$  find functions  $A_1, A_2, \dots A_n \dots$  such that

$$\left( 1 + \frac{l^2}{n^2\pi^2} \frac{\partial}{\partial t} \right) A_n = E \quad (66)$$

hence

$$A_n = E \left( 1 + a_n e^{-K \frac{n^2\pi^2}{l^2} t} \right) \quad (67)$$

Using these values for  $A_1, A_2, \dots$  in a manner similar to the quantities  $x_r^{(\alpha)}, x_r^{(\beta)}$ , etc., in (23), it is now possible to get an infinite series of equations for  $C_1$  and its derivatives corresponding to equations (24) in the finite case. Assuming that the method of elimination holds when the number of equations becomes infinite, the value of  $C_1$  obtained is

$$C_1 = E \left[ \alpha + \sum_1^\infty \beta_n e^{-K \frac{n^2\pi^2}{l^2} t} \right] \quad (68)$$



where  $\alpha, \beta_1, \beta_2, \dots, \beta_n, \dots$  are arbitrary constants. Substituting this value of  $C_1$  in equation (61) and performing the operations indicated there, on collecting terms it will be found that

$$v = E \left[ \alpha x + \sum_1^{\infty} \beta'_n e^{-K \frac{n^2 \pi^2 t}{l^2}} \sin \frac{n\pi}{l} x \right] \quad (69)$$

To determine  $\alpha$ , it is known when the steady state is reached, i.e., when  $t = \infty$ .

$$(v)_{t=\infty} = E \frac{x}{l} \quad (70)$$

Hence  $\alpha = \frac{1}{l}$ . This result might also have been obtained by tracing through the eliminations from (67) to (68), but this was not necessary.

Finally the last condition in (58) gives  $v = 0$  when  $t = 0$ ; hence

$$-\frac{Ex}{l} = \sum_1^{\infty} \beta'_n \sin \frac{n\pi}{l} x \quad (71)$$

and from this the values of the constants  $\beta'_n \dots$  can be obtained by the usual Fourier series method.

It may be interesting to compare this with Heaviside's method. He writes equation (57) in the form<sup>9</sup>

$$K \frac{\partial^2 v}{\partial x^2} = pv$$

the solution of which is by ordinary methods

$$v = A \cosh \sqrt{\frac{p}{K}} x + B \sinh \sqrt{\frac{p}{K}} x.$$

Then since  $v = 0$  when  $x = 0$ ,  $A = 0$ , and since  $v = E$  when  $x = l$ ,

$$B = \frac{E}{\sinh \sqrt{\frac{p}{K}} l}.$$

Hence

$$v = \frac{E \sinh \sqrt{\frac{p}{K}} x}{\sinh \sqrt{\frac{p}{K}} l}.$$

---

<sup>9</sup> Heaviside, "Electromagnetic Theory," vol. 2, p. 138 *et seq.*, except for some slight changes in notation and terminal conditions.



It is evident this equation corresponds to the quotient of (61) by (62). Heaviside's determination of the roots of  $\sinh \sqrt{\frac{p}{K}}l$  then corresponds to writing equation (62) in the factorial form (65) and the summation over these roots in the expansion theorem corresponds to the solving of equations of the type (66) and the subsequent eliminations. It may be noticed that in solving the equations (66) two methods are available: (a) let  $a_1, a_2, \dots a_n \dots$  in (67) be undetermined constants whose values are determined later, as has been done above; (b) assume that Heaviside's terminal conditions hold so that the value of each of the constants  $a_1, a_2, \dots a_n \dots$  is  $-1$ . Then, on carrying out the elimination, a value for  $C_1$  is obtained which does not contain any unknown constants, and knowing  $C_1$ ,  $v$  is obtained from (61).

Following Heaviside it will be found very convenient in subsequent work to use a symbolical notation for the series developments that arise. It is not necessary to do so, but it will be found to curtail considerably the labor of writing. For example, (61) may be written,

$$\frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \left[ x \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} + \frac{x^3}{3!} \left( \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right)^3 + \frac{x^5}{5!} \left( \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right)^5 + \dots \right] C_1 \tag{72}$$

and this by analogy with the expansion for  $\sinh n\theta$ , can be denoted symbolically by

$$\frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left( x \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right) C_1 \tag{72a}$$

The factor  $\frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}}$  in front gives rise to no difficulty, as it cancels out again when the sinh term is written in the factorial form

$$x \left( 1 + \frac{x^2}{\pi^2} \frac{\partial}{\partial t} \right) \left( 1 + \frac{x^2}{2^2 \pi^2} \frac{\partial}{\partial t} \right) \dots \left( 1 + \frac{x^2}{n^2 \pi^2} \frac{\partial}{\partial t} \right) \dots C_1 \tag{72b}$$



The following abbreviations which will be required later are now self-evident.

$$\cosh \left( x \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right) C_1 = \left( 1 + \frac{x^2}{2!} \frac{1}{K} \frac{\partial}{\partial t} + \frac{x^4}{4!} \frac{1}{K^2} \frac{\partial^2}{\partial t^2} + \dots \right) C_1 \quad (73)$$

and

$$J_n \left( x \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right) C_1 = \frac{x^n}{2^n \Gamma(n+1)} \left[ 1 - \frac{x^2}{2(2n+2)} \frac{1}{K} \frac{\partial}{\partial t} + \frac{x^4}{2 \cdot 4(2n+2)(2n+4)} \frac{1}{K^2} \frac{\partial^2}{\partial t^2} + \dots \right] C_1 \quad (74)$$

where the factor  $z_0$  in (55) has been replaced by  $\frac{1}{2^n \Gamma(n+1)}$  to conform to the standard expression for the Bessel function. Both (73) and (74) can be written in a factorial form analogous to (72b).

#### FLOW OF HEAT IN A SEMI-INFINITE SOLID.

As the solution for an infinite or semi-infinite solid is usually given in the form of an integral instead of an infinite series, it may be well to show how this result is arrived at. The equations for the flow of heat in a semi-infinite solid are

$$K \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \quad (75)$$

$$\left. \begin{aligned} v &= f(x) \text{ when } t = 0 \\ v &= 0 \text{ when } x = 0 \\ v &= 0 \text{ when } x = \infty \end{aligned} \right\} \quad (75a)$$

Solving these equations in a manner similar to that used in the last example, and using the last condition in (75a) in the form  $v = 0$  when  $x = l$  as  $l$  tends to infinity. The result is <sup>10</sup>

$$v = \lim_{l \rightarrow \infty} \sum_{n=1}^{\infty} e^{-K \frac{n^2 \pi^2}{l^2} t} \sin \frac{n\pi}{l} x \cdot \frac{2}{l} \int_0^l f(x') \sin \frac{n\pi}{l} x' dx' \quad (76)$$

and as  $l \rightarrow \infty$  this can be written as an integral, putting  $\frac{\pi}{l} = d\alpha$

$$v = \frac{2}{\pi} \int_0^{\infty} e^{-K\alpha^2 t} \sin \alpha x \int_0^{\infty} f(x') \sin \alpha x' dx' d\alpha \quad (76a)$$

<sup>10</sup> See Carslaw, "Introduction to Theory of Conduction of Heat," 1921, p. 35.



which corresponds with the expression given by Carslaw (*loc. cit.*). This again can be transformed as shown by him to the more standard form

$$v = \frac{1}{2\sqrt{\pi K t}} \int_0^\infty f(x') \left[ e^{-\frac{(x-x')^2}{4Kt}} - e^{-\frac{(x+x')^2}{4Kt}} \right] dx'$$

#### FOURIER'S RING.

In order to illustrate the application of the method to Bessel functions, it is first necessary to solve the problem of Fourier's Ring. In this case the equations for the temperature are

$$K \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \quad (t > 0, -\pi < x < \pi) \quad (77)$$

$$v = f(x) \quad (t = 0, -\pi < x < \pi) \quad (78)$$

$$\left. \begin{aligned} (v)_{x=\pi} &= (v)_{x=-\pi} \\ \left(\frac{\partial v}{\partial x}\right)_{x=\pi} &= \left(\frac{\partial v}{\partial x}\right)_{x=-\pi} \end{aligned} \right\} \quad (79)$$

Integrating (77) from  $-\pi$  to  $x$ ,

$$\frac{\partial v}{\partial x} = \left(\frac{\partial v}{\partial x}\right)_{x=-\pi} + \frac{1}{K} \int_{-\pi}^x \frac{\partial v}{\partial t} dx \quad (80)$$

Integrating again

$$v = C + C_1(x + \pi) + \frac{1}{K} \int_{-\pi}^x \int_{-\pi}^x \frac{\partial v}{\partial t} dx dx. \quad (81)$$

where  $C = (v)_{x=-\pi}$  and  $C_1 = \left(\frac{dv}{dx}\right)_{x=-\pi}$  are functions of  $t$  alone. Solving this integral equation, the result may be written

$$v = \cosh \left[ (x + \pi) \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left[ (x + \pi) \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (82)$$

Putting  $x = 0$  in this expression

$$(v)_{x=0} = \cosh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (83)$$

Returning again to equation (77) and integrating from  $+\pi$  to  $x$ , the result is obtained,

$$v = \cosh \left[ (x - \pi) \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left[ (x - \pi) \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (84)$$



where  $C$  and  $C_1$  are the same as in (82) on account of the relations (79). Putting  $x = 0$  in (84)

$$(v)_{x=0} = \cosh \left[ -\pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \frac{1}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left[ -\pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (85)$$

Subtracting (85) from (83), the cosh terms disappear and

$$0 = \frac{2}{\sqrt{\frac{1}{K} \frac{\partial}{\partial t}}} \sinh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (86)$$

Writing this in the factorial form

$$0 = \pi \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{\pi^2} \right) \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{2^2 \pi^2} \right) \dots \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{n^2 \pi^2} \right) \dots C_1 \quad (87)$$

and finding functions  $A_1, A_2, \dots, A_n, \dots$  such that

$$\left( 1 + \frac{1}{K} \frac{\partial}{\partial t} \right) A_n = 0 \quad (88)$$

giving

$$A_n = a_n e^{-Kn^2 t} \quad (89)$$

then on applying the method of elimination

$$C_1 = \sum_1^{\infty} a'_n e^{-Kn^2 t} \quad (90)$$

where  $a'_1, a'_2, \dots, a'_n, \dots$  are some new constants.

Again, on differentiating (82) and (84) with respect to  $x$ , and putting  $x = 0$  in the result,

$$\left( \frac{\partial v}{\partial x} \right)_{x=0} = \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \sinh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \cosh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (91)$$

and

$$\left( \frac{\partial v}{\partial x} \right)_{x=0} = \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \sinh \left[ -\pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C + \cosh \left[ -\pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C_1 \quad (92)$$

Subtracting these equations,

$$0 = 2 \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \sinh \left[ \pi \sqrt{\frac{1}{K} \frac{\partial}{\partial t}} \right] C \quad (93)$$

Writing this in the factorial form

$$0 = \frac{x}{K} \frac{\partial}{\partial t} \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{\pi^2} \right) \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{2^2 \pi^2} \right) \dots \left( 1 + \frac{\pi^2 \frac{1}{K} \frac{\partial}{\partial t}}{n^2 \pi^2} \right) \dots C \quad (94)$$



This is identical with equation (87) except for the extra factor  $\frac{\partial}{\partial t}$  in front. This gives rise to a constant term in addition to the exponential, hence,

$$C = \sum_0^{\infty} b'_n e^{-Kn^2t} \quad (95)$$

Substituting the values of  $C$  and  $C_1$  from (95) and (90) in (81), the value of  $v$  is obtained after some obvious simplifications in the standard form

$$v = \sum_0^{\infty} (\alpha_n \cos nx + \beta_n \sin nx) e^{-Kn^2t} \quad (96)$$

where  $\alpha_n$  and  $\beta_n$  are determined in the usual manner from (78).

It may be remarked in connection with the subtraction\* and differentiation of the symbolic sines and cosines, etc., above, that these operations must be justified by recourse to the infinite series they represent. It will readily be noticed, however, that they follow the usual laws for these expressions.

#### FLOW OF HEAT IN AN INFINITE CYLINDER.

This example will illustrate the application to Bessel's function. Let the surface  $r=a$  be kept at zero temperature, and the initial temperature be  $v=f(r, \theta)$ . The equation of conduction in this case is

$$\frac{\partial v}{\partial t} = K \left( \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v}{\partial \theta^2} \right) \quad (97)$$

Writing this equation

$$\frac{\partial^2 v}{\partial \theta^2} = \frac{r^2}{K} \frac{\partial v}{\partial t} - r^2 \frac{\partial^2 v}{\partial r^2} - r \frac{\partial v}{\partial r} \quad (98)$$

the same conditions hold for integration with respect to  $\theta$ , as in the case of Fourier's ring, *i.e.*,

$$(v)_{\theta=\pi} = (v)_{\theta=-\pi} \quad (99)$$

$$\left( \frac{\partial v}{\partial \theta} \right)_{\theta=\pi} = \left( \frac{\partial v}{\partial \theta} \right)_{\theta=-\pi} \quad (100)$$

Hence proceeding as in that example

$$v = \cosh \left[ (\theta + \pi) \sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}} \right] C \\ + \frac{1}{\sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}}} \sinh \left[ (\theta + \pi) \sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}} \right] C_1 \quad (101)$$



and the equations analogous to (86) and (93) become,

$$0 = \frac{2}{\sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}}} \sinh \left[ \pi \sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}} \right] C_1 \quad (102)$$

and

$$0 = 2 \sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}} \sinh \left[ \pi \sqrt{\frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r}} \right] C \quad (103)$$

where

$$C = (v)_{\theta=\pi} \text{ and } C_1 = \left( \frac{\partial v}{\partial \theta} \right)_{\theta=\pi}$$

Writing (102) in the factorial form it becomes

$$0 = 2\pi \left( 1 + \frac{\pi^2 \left( \frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r} \right)}{\pi^2} \right) \dots \left( 1 + \frac{\pi^2 \left( \frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r} \right)}{n^2 \pi^2} \right) \dots C_1 \quad (104)$$

and in order to apply the method of elimination functions  $A_1, A_2, \dots, A_n, \dots$  must be found such that

$$\left[ 1 + \frac{\pi^2 \left( \frac{r^2}{K} \frac{\partial}{\partial t} - r^2 \frac{\partial^2}{\partial r^2} - r \frac{\partial}{\partial r} \right)}{n^2 \pi^2} \right] A_n = 0. \quad (105)$$

or

$$\frac{\partial^2 A_n}{\partial r^2} + \frac{1}{r} \frac{\partial A_n}{\partial r} + \left( -\frac{1}{K} \frac{\partial}{\partial t} - \frac{n^2}{r^2} \right) A_n = 0. \quad (106)$$

Solving this by the integral equation method already outlined in (50) *et seq.*,

$$A_n = J_n \left( r \sqrt{-\frac{1}{K} \frac{\partial}{\partial t}} \right) B \quad (107)$$

where  $B = (A_n)_{r=0}$  is a function of  $t$  alone.

By applying the method of elimination to (104) the value obtained for  $C_1$  would be  $\sum_1^{\infty} a_n A_n$  and in a similar manner from (103)  $C$  could be expressed as  $\sum_1^{\infty} a'_n A'_n$ . Substitution in (101) of these values gives

$$v = \sum_1^{\infty} a_n A_n f_n(\theta) + \sum_1^{\infty} a'_n A'_n f'_n(\theta) \quad (108)$$



where  $A_n$  and  $A'_n$  are functions of  $r$  and  $t$  alone. But from the terminal conditions  $v = 0$  when  $r = a$ . Hence when  $r = a$ ,  $A_n$  and  $A'_n$  must both equal zero, since they are functions of  $t$ , and the presence of the arbitrary constants  $a_n$  and  $a'_n$  in (108) requires that each individual  $A_n$  vanish, instead of the coefficients of the various powers of  $t$ , which is more usually the case. Hence putting  $r = a$  in (107),

$$0 = J_n \left( a \sqrt{-\frac{1}{K} \frac{\partial}{\partial t}} \right) B \quad (109)$$

It is known that  $J_n(a\alpha)$  possesses equal positive and negative roots, and if the positive roots are  $\alpha_1, \alpha_2, \dots, \alpha_s, \dots$ , equation (109) can be written in the factorial form,

$$0 = Q \left[ 1 + \frac{\frac{1}{K} \frac{\partial}{\partial t}}{\alpha_1^2} \right] \left[ 1 + \frac{\frac{1}{K} \frac{\partial}{\partial t}}{\alpha_2^2} \right] \dots \left[ 1 + \frac{\frac{1}{K} \frac{\partial}{\partial t}}{\alpha_s^2} \right] \dots B \quad (110)$$

where  $Q$  is some constant. This equation which is similar to (87) has the solution,

$$B = \sum_1^{\infty} p_s e^{-K\alpha_s^2 t}$$

where  $p_1, p_2, \dots, p_s, \dots$  are arbitrary constants. Substituting this value of  $B$  in equation (107) when written in the form

$$A_n = r^n \left[ 1 + \frac{r^2 \frac{1}{K} \frac{\partial}{\partial t}}{2(2n+2)} + \frac{r^4 \frac{1}{K^2} \frac{\partial^2}{\partial t^2}}{2 \cdot 4(2n+2)(2n+4)} + \dots \right] \sum_1^{\infty} p_s e^{-K\alpha_s^2 t} \quad (111)$$

and performing the operations, it becomes

$$A_n = \sum_{s=1}^{\infty} p'_s J_n(\alpha_s r) e^{-K\alpha_s^2 t} \quad (112)$$

From (104) and (106)

$$C_1 = \sum_{n=1}^{\infty} p''_s A_n$$

Hence

$$C_1 = \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} p_{n,s} J_n(\alpha_s r) e^{-K\alpha_s^2 t} \quad (113)$$

In a similar manner the value of  $C$  is found from (103).

$$C = \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} q_{n,s} J_n(\alpha_s r) e^{-K\alpha_s^2 t} \quad (114)$$



Substituting these values of  $C$  and  $C_1$  in equation (101), written out in the power series expansion and performing the differentiations indicated, the final result is obtained in the standard form

$$v = \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \left( A_{n,s} \cos n\theta + B_{n,s} \sin n\theta \right) J_n(\alpha_s r) e^{-K\alpha_s^2 t} \quad (115)$$

where  $A_{n,s}$  and  $B_{n,s}$  are determined in the usual way from the condition  $v = f(r, \theta)$  when  $t = 0$ .

Several more examples of heat problems could be given, but those derived here should suffice to show the general method of procedure. For problems in the flow of electricity in continuous systems, Heaviside's Electromagnetic Theory will supply many results already worked out, which can be easily modified in accordance with the suggestions made at the end of the problem of a cable with resistance and capacity.

#### APPLICATION TO POTENTIAL PROBLEMS.

The similarity between the equations of conduction of heat and Laplace's equation suggests that this method might be used to solve potential problems. Its application, however, is accompanied by difficulties which are mainly due to the way in which the boundary conditions are stated. The following examples will make this clear.

##### THE POTENTIAL DUE TO TWO CONDUCTING PLANES INTERSECTING

AT AN ANGLE  $\frac{\pi}{p}$ .

Assume there is no variation in the  $z$  direction, then  $\frac{\partial^2 V}{\partial z^2} = 0$  and Laplace's equation in cylindrical coördinates may be written,

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{1}{r^2} \frac{\partial^2 V}{\partial \phi^2} = 0 \quad (116)$$

subject to the conditions

$$\left. \begin{aligned} V &= V_0 \text{ when } \phi = 0 \\ V &= V_0 \text{ when } \phi = \frac{\pi}{p} \end{aligned} \right\} \quad (117)$$

If  $r \frac{d}{dr}$  is replaced by  $D_r$ , equation (116) may be written

$$\frac{\partial^2 V}{\partial \phi^2} = -D_r^2 V \quad (118)$$

integrating twice with respect to  $\phi$

$$V = V_0 + C\phi - \int_0^\phi \int_0^\phi D_r^2 V d\phi d\phi \quad (119)$$



where  $C = \left(\frac{\partial V}{\partial \phi}\right)_{\phi=0}$  is a function of  $r$  alone, and  $V_0$  is the value of  $V$  when  $\phi = 0$ .  $V_0$  being thus a constant independent of  $r$  and  $\phi$  does not give rise to a series of terms when the integral equation (119) is solved by successive approximations due to the presence of the differentiator  $D_r^2$  under the integral sign. The solution of (119) becomes

$$V = V_0 + C\phi - \frac{\phi^3}{3!} D_r^2 C + \frac{\phi^5}{5!} D_r^4 C - \text{etc.}$$

(120)

or symbolically

$$V = V_0 + \frac{1}{D_r} \sin(\phi D_r) C$$

(121)

but from (117)  $V = V_0$  when  $\phi = \frac{\pi}{p}$ . Substituting in (121) gives

$$0 = \frac{1}{D_r} \sin\left(\frac{\pi}{p} D_r\right) C$$

(122)

which may be written in the form of an infinite product,

$$0 = \frac{\pi}{p} \left(1 - \frac{\pi^2 D_r^2}{p^2 \pi^2}\right) \left(1 - \frac{\pi^2 D_r^2}{2^2 \pi^2}\right) \cdots \left(1 - \frac{\pi^2 D_r^2}{n^2 \pi^2}\right) \cdots C$$

(123)

In order to apply the method of elimination, functions  $a_1, a_2, \dots a_n \dots$  must be found such that

$$\left(1 - \frac{\pi^2 D_r^2}{n^2 \pi^2}\right) a_n = 0$$

(124)

or

$$r \frac{\partial}{\partial r} \left(r \frac{\partial a_n}{\partial r}\right) - p^2 n^2 a_n = 0$$

(125)

the solution of which is

$$a_n = A_n r^{pn} + B_n r^{-pn}$$

(126)

Hence by elimination (123) gives

$$C = \sum_{n=1}^{n=\infty} (A'_n r^{pn} + B'_n r^{-pn})$$

(127)

where  $A'_n$  and  $B'_n$  are some arbitrary constants.

Substituting this value of  $C$  in (120) and simplifying

$$V = V_0 + \sum_{n=1}^{n=\infty} (A''_n r^{pn} + B''_n r^{-pn}) \sin pn \theta$$

(128)



Now since  $V = V_0$  when  $r = 0$  each of the coefficients  $B''_1, B''_2, \dots, B''_n, \dots$  must be zero, hence

$$V = V_0 + \sum_{n=1}^{n=\infty} A''_n r^{pn} \sin pn\theta \quad (129)$$

Another boundary condition is required to determine the remaining constants. This will be taken to be that the potential over the sphere at infinity is a constant, and equal to  $V_1$ . Hence

$$V_1 = V_0 + \lim_{l \rightarrow \infty} \sum_{n=1}^{n=\infty} A''_n l^{pn} \sin pn\theta \quad (130)$$

or

$$\lim_{l \rightarrow \infty} \left( \frac{V_1}{l^p} - \frac{V_0}{l^p} \right) = \lim_{l \rightarrow \infty} \left( A''_1 \sin p\theta + A''_2 l^p \sin 2p\theta + \dots \right) \quad (131)$$

Now  $V_0$  is some finite quantity so that  $\frac{V_0}{l^p}$  tends to zero as  $l \rightarrow \infty$ .

If it is also assumed that  $V_1$  is finite,  $\frac{V_1}{l^p}$  tends to zero at the same time, so that all the coefficients are zero and the solution becomes trivial. If, however,  $\frac{V_1}{l^p}$  tends to a constant finite value  $R$  as  $l \rightarrow \infty$ , then

$$R = A''_1 \sin p\theta + A''_2 l^p \sin 2p\theta + A''_3 l^{2p} \sin 3p\theta + \dots \quad (132)$$

and this holds for  $0 < \theta < \frac{\pi}{p}$ , and for the limit  $l \rightarrow \infty$ .

By comparing this series with the expansion

$$\frac{\pi}{4} = \sin x + \frac{\sin 3x}{3} + \frac{\sin 5x}{5} + \dots \quad (133)$$

which is valid in the region  $0 < x < \pi$  the following equations are obtained where the limit  $l \rightarrow \infty$  is understood,

$$\begin{array}{lll} A''_1 = k & A''_3 l^{2p} = \frac{1}{3} k & A''_5 l^{4p} = \frac{1}{5} k \\ A''_2 = 0 & A''_4 = 0 & A''_6 = 0 \end{array} \quad \text{etc.}$$

where  $k$  is a constant. Hence from (129)

$$V = V_0 + \lim_{l \rightarrow \infty} \left( k r^p \sin p\theta + \frac{k}{3 l^{2p}} r^{3p} \sin 3p\theta + \dots \right) \quad (134)$$

or

$$V = V_0 + k r^p \sin p\theta \quad (135)$$

If  $V = 0$  and  $k = 1$ , this becomes

$$V = r^p \sin p\theta \quad (136)$$

which corresponds with the well-known result.



Equation (136), however, does not give a constant potential over the sphere at infinity, which was assumed as one of the boundary conditions. The explanation is seen in (134). For all finite values of  $r$  this is equal to (135), but when  $r=l$  and both approach the value infinity, the value of (134) becomes

$$V = V_0 + \lim_{r \rightarrow \infty} r^p \times \text{a constant.} \quad (137)$$

The usual method of deriving (136) by conformal representation does not show that this limitation exists.

THE GREEN'S FUNCTION FOR THE SPACE BOUNDED BY TWO PARALLEL PLANES  $z = 0$  AND  $z = C > 0$ .

Take Laplace's equation in cylindrical coördinates  $z, \rho, \theta$ . Let the pole be at the point  $z', 0, 0$ , and since there is circular symmetry  $\frac{\partial V}{\partial \theta} = 0$ , so that Laplace's equation becomes

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{\partial^2 V}{\partial z^2} = 0 \quad (138)$$

Integrating with respect to  $z$ ,

$$\frac{\partial V}{\partial z} - \left( \frac{\partial V}{\partial z} \right)_{z=0} = - \int_0^z \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) V dz \quad (139)$$

writing  $\left( \frac{\partial V}{\partial z} \right)_{z=0} = R$  which is a function of  $r$  alone, and integrating again

$$V = Rz - \int_0^z \int_0^z \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) V dz dz \quad (140)$$

since  $(V)_{z=0} = 0$ . This has the solution

$$V = \frac{1}{\sqrt{\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}}} \sin \left( z \sqrt{\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}} \right) R \quad (141)$$

But  $(V)_{z=C} = 0$ , so that this equation can be solved by finding functions  $A_1, A_2, \dots, A_n, \dots$  such that

$$\left[ 1 - \frac{C^2 \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right)}{n^2 \pi^2} \right] A_n = 0 \quad (142)$$

or

$$\frac{\partial^2 A_n}{\partial r^2} + \frac{1}{r} \frac{\partial A_n}{\partial r} - \frac{n^2 \pi^2}{C^2} A_n = 0 \quad (143)$$



The solution of this equation which has a zero at infinity is

$$A_n = K_0 \left( \frac{n\pi}{C} r \right) \quad (144)$$

Hence by elimination

$$V = \sum_1^{\infty} a_n \sin \frac{n\pi}{C} z K_0 \left( \frac{n\pi}{C} r \right) \quad (145)$$

where the constants  $a_n$  have to be determined from the fact that when  $z = z'$ , and  $r$  is very small, the value of  $V$  tends to  $\frac{1}{r} -$  a constant.

Now a well-known integral is

$$\frac{2}{\pi} \int_0^{\infty} \cos \alpha z K_0(\alpha \rho) d\alpha = \frac{1}{(\rho^2 + z^2)^{\frac{1}{2}}} \quad (146)$$

which becomes, when  $z = 0$ ,

$$\int_0^{\infty} K_0(\alpha \rho) d\alpha = \frac{\pi}{2} \frac{1}{\rho} \quad (147)$$

If in (145)  $a_n$  is taken equal to  $\frac{1}{\sin \frac{n\pi}{C} z'}$ , then putting  $z = z'$  in

this equation, and making  $r$  very small, it can be written

$$V_{\text{pole}} = \lim_{r \rightarrow 0} \sum_1^{\infty} \frac{1}{\frac{\pi r}{C}} K_0 \left( n \frac{\pi r}{C} \right) \cdot \frac{\pi r}{C} \quad (148)$$

$$= \frac{C}{\pi r} \int_0^{\infty} K_0(\alpha) d\alpha = \frac{C}{2r}. \quad (149)$$

Hence

$$V = \frac{2}{C} \sum_1^{\infty} \frac{\sin \frac{n\pi}{C} z}{\sin \frac{n\pi}{C} z'} K_0 \left( \frac{n\pi}{C} r \right) \quad (150)$$

would give an expression which satisfies the conditions for a Green's function. Owing, however, to the presence of  $\sin \frac{n\pi}{C} z'$  in the denominator, there will in general be other infinities, which



makes it desirable to find another form. To do this put  $dn = \sin \frac{n\pi}{C} z'$ . Then (145) becomes when  $z = z'$  and  $r \rightarrow 0$ ,

$$\begin{aligned} V_{\text{pole}} &= \lim_{r \rightarrow 0} \frac{1}{2 \frac{\pi r}{C}} \sum_1^{\infty} \left( 1 - \cos \frac{2n\pi}{C} z' \right) K_0 \left( n \frac{\pi r}{C} \right) \frac{\pi r}{C} \\ &= \lim_{r \rightarrow 0} \left[ \frac{C}{4r} - \frac{C}{2\pi r} \sum_1^{\infty} \cos \left( \frac{n\pi r}{C} \cdot \frac{2z'}{r} \right) K_0 \left( n \frac{\pi r}{C} \right) \frac{\pi r}{C} \right] \quad (151) \\ &= \lim_{r \rightarrow 0} \left[ \frac{C}{4r} - \frac{C}{2\pi r} \int_0^{\infty} \cos \left( \alpha \frac{2z'}{r} \right) K_0(\alpha) d\alpha \right] \\ &= \lim_{r \rightarrow 0} \left[ \frac{C}{4r} - \frac{C}{2\pi r} \cdot \frac{\pi}{2} \cdot \frac{1}{\left( 1 + \frac{4z'^2}{r^2} \right)^{\frac{1}{2}}} \right] \\ &= \lim_{r \rightarrow 0} \left[ \frac{C}{4r} - \frac{C}{8z'} \right] \quad (152) \end{aligned}$$

Hence

$$V = \frac{4}{C} \sum_1^{\infty} \sin \frac{n\pi}{C} z' \sin \frac{n\pi}{C} z K_0 \left( \frac{n\pi}{C} r \right) \quad (153)$$

is a suitable expression for the Green's function.<sup>11</sup>

#### THE POTENTIAL BETWEEN TWO PARALLEL CONDUCTING PLANES GIVEN BY

$$x = 0 \text{ AND } x = 1.$$

This example is taken to show the failure of the method and suggest a possible approximate solution. Take Laplace's equation in rectangular coördinates,

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \quad (154)$$

The conditions of integration are

$$\left. \begin{aligned} V &= V_0 \text{ when } x = 0 \\ V &= V_1 \text{ when } x = 1 \end{aligned} \right\} \quad (155)$$

Integrating (154) in the usual manner with respect to  $x$

$$V = V_0 + Cx - \int_0^x \int_0^x \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) V dx dx \quad (156)$$

the solution of which may be written symbolically

$$V = V_0 + \frac{1}{\sqrt{\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}} \sin \left( x \sqrt{\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}} \right) C \quad (156a)$$

<sup>11</sup> Cf. Gray and Matthews, "Bessel Functions," 1922, 2nd ed., p. 104.



where  $C = \left( \frac{\partial V}{\partial x} \right)_{x=0}$ . Putting  $x=l$  and writing this equation in the factorial form, it becomes

$$V_1 - V_0 = l \left( 1 - \frac{l^2 \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}{\pi^2} \right) \left( 1 - \frac{l^2 \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}{2^2 \pi^2} \right) \dots C \quad (157)$$

To solve this, functions  $a_1, a_2, \dots a_n \dots$  must be found such that

$$\left( 1 - \frac{l^2 \left( \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)}{n^2 \pi^2} \right) a_n = V_1 - V_0 \quad (158)$$

or

$$\frac{\partial^2 a_n}{\partial y^2} + \frac{\partial^2 a_n}{\partial z^2} - \frac{n^2 \pi^2}{l^2} a_n = (V_0 - V_1) \frac{n^2 \pi^2}{l^2} \quad (159)$$

Integrating with respect to  $y$

$$a_n = (V_0 - V_1) + (a_n)_{y=0} + \left( \frac{\partial a_n}{\partial y} \right)_{y=0} y + \int_0^y \int_0^y \left( \frac{n^2 \pi^2}{l^2} - \frac{\partial^2}{\partial z^2} \right) a_n dy dy \quad (160)$$

which on solution by the method of successive approximations gives

$$\begin{aligned} a_n = & (V_0 - V_1) + \cosh \left( y \sqrt{\frac{n^2 \pi^2}{l^2} - \frac{\partial^2}{\partial z^2}} \right) (a_n)_{y=0} \\ & + \frac{1}{\sqrt{\frac{n^2 \pi^2}{l^2} - \frac{\partial^2}{\partial z^2}}} \sinh \left( y \sqrt{\frac{n^2 \pi^2}{l^2} - \frac{\partial^2}{\partial z^2}} \right) \left( \frac{\partial a_n}{\partial y} \right)_{y=0} \end{aligned} \quad (161)$$

Now (161) is a differential equation containing two variables,  $(a_n)_{y=0}$  and  $\left( \frac{\partial a_n}{\partial y} \right)_{y=0}$ , both functions of  $z$ . Hence another equation is required. It would seem as if this could be obtained from the conditions that with charges in the finite portion of space, the potential at infinity in both positive and negative directions must be zero. This would supply two conditions, one of which might be used in (160) if the integration were taken from  $-l$  to  $y$ , then as  $l$  tends to infinity  $(a_n)_{y=-l}$  tends to zero. Equation (161) would then have only one variable  $\left( \frac{\partial a_n}{\partial y} \right)_{y=-l}$  and putting  $y = +l$  in this equation, the method of elimination could be used to determine  $\left( \frac{\partial a_n}{\partial y} \right)_{y=-l}$ . On taking the limit of the series thus obtained as  $l$  tends to infinity, it will be found to be expressible as a definite integral similar to that obtained in the example of



flow of heat in a semi-infinite solid. This will not be done here, however, as the difficulty which the determination of the constants in the final result presents, can be illustrated as well in the two dimensional case as in the three dimensional problem. In the case of two dimensions  $\frac{\partial^2 V}{\partial z^2} = 0$ , hence (159) may be written,

$$\frac{\partial^2 a_n}{\partial y^2} = \frac{n^2 \pi^2}{l^2} (a_n + V_0 - V_1) \quad (162)$$

The solution of which is

$$a_n = V_1 - V_0 + A_n \cosh \frac{n\pi}{l} y + B_n \sinh \frac{n\pi}{l} y \quad (163)$$

Hence from (157)

$$C = K(V_1 - V_0) + \sum_{n=1}^{\infty} \left( A_n'' \cosh \frac{n\pi}{l} y + B_n'' \sinh \frac{n\pi}{l} y \right) \quad (164)$$

and substituting this value of  $C$  in (156a)

$$V = V_0 + K'(V_1 - V_0)x + \sum_{n=1}^{\infty} \left( A_n'' \cosh \frac{n\pi}{l} y + B_n'' \sinh \frac{n\pi}{l} y \right) \sin \frac{n\pi}{l} x \quad (165)$$

and since the solution obtained must tend to zero as  $y \rightarrow \infty$  by expanding the hyperbolic sines and cosines, it is found that if the

$e^{\frac{n\pi}{l} y}$  terms disappear  $A_n'' = -B_n''$ , giving

$$V = V_0 + K'(V_1 - V_0) + \sum_1^{\infty} A_n'' e^{-\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \quad (166)$$

for  $y > 0$  and similarly

$$V = V_0 + K'(V_1 - V_0) + \sum_1^{\infty} A_n'' e^{\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \quad (167)$$

for  $y < 0$ .

If  $V_0$  and  $V_1$  both equal zero, then for  $y > 0$

$$V = \sum_1^{\infty} A_n'' e^{-\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \quad (168)$$

The determination of the constants  $A_n''$  presents the real difficulty. So far nothing has been said of the disposition of the charges or



charged conductors in the field. Suppose that, for instance, the cylinder represented by

$$(x - \alpha)^2 + (y - \beta)^2 = \delta^2$$

has a potential  $V_c$  and there are no other charges in the space. It seems as if this condition should suffice to determine analytically the values of the constants, but the problem of doing this has apparently not been solved. An approximate method, however, suggests itself. Let  $p$  points be taken on the surface of this cylinder. Then if the  $p$  values of  $x$  and  $y$  for these points are substituted in (168) and the first  $p$  terms of the series taken, the values of the coefficients  $A_1 \dots A_p$  could be obtained from the  $p$  equations; and provided the terms decrease in regular order, and the last term is small, this would give an approximate solution which could be used in the region where the value of the last term remained small enough to be negligible. Similarly if a line charge is placed at  $x', y'$ , by surrounding this with a small cylinder, the potential on this cylinder will be practically uniform and equal to  $\frac{1}{r}$ , where  $r$  is the distance from  $x', y'$ , if there are no other charges present. From the value of the potential at  $p$  points on this circumference the values of the coefficients might be determined as above. When several conductors are in the space, by taking sufficient numbers of points on each of them, it is probable that fairly good approximations might be obtained. This will, however, have to be tested by actual numerical work in known cases, to determine the value of the method.

#### EVALUATION OF DEFINITE INTEGRALS.

The operators which have been developed earlier in this work may sometimes be of use in determining the values of definite integrals. Take, for example,

$$I = \int_0^\infty e^{-xt} J_0(bx) dx \quad (169)$$

When  $n = 0$  equation (56) becomes with a slight change in notation

$$\left(1 + x^2 \int_0^b \frac{1}{b} \int_0^b b \, db \, db\right) J_0(bx) = 1$$

so that if it is possible to introduce this operator under the integral sign, the Bessel function will be replaced by unity, and the integral



$\int_0^\infty e^{-xt} dx$  is then easily found. Differentiating (169) twice with respect to  $t$  gives

$$\frac{\partial^2 I}{\partial t^2} = \int_0^\infty x^2 e^{-xt} J_0(bx) dx \quad (170)$$

Hence

$$\begin{aligned} I + \int_0^b \frac{1}{b} \int_0^b b \frac{\partial^2 I}{\partial t^2} db db &= \int_0^\infty e^{-xt} \left[ \left( 1 + x^2 \int_0^b \frac{1}{b} \int_0^b b db db \right) J_0(bx) \right] dx \\ &= \int_0^\infty e^{-xt} dx = \frac{1}{t} \end{aligned} \quad (171)$$

Therefore

$$I = \frac{1}{t} - \int_0^b \frac{1}{b} \int_0^b b \frac{\partial^2 I}{\partial t^2} db db \quad (172)$$

and on solving this by successive approximations

$$\begin{aligned} I &= \frac{1}{t} - \frac{b^2}{2^2} \frac{2!}{t^3} + \frac{b^4}{2^2 \cdot 4^2} \frac{4!}{t^5} - \frac{b^6}{2^2 \cdot 4^2 \cdot 6^2} \frac{6!}{t^7} + \dots \\ &= \frac{1}{(t^2 + b^2)^{\frac{1}{2}}} \end{aligned}$$

which is a well-known result.

In volume 3, p. 234 *et seq.*, of "Electromagnetic Theory," Heaviside gives a method of finding integrals in a similar manner, which is in fact very much shorter than the one just outlined. He uses, however, the opposite operator to the one used above, *i.e.*, he uses an operator which transforms a constant into the Bessel function, and as this involves the use of his "unit function," it cannot be discussed here. Several examples will be found in his book.

#### CONCLUSION.

The examples which have been worked out should be sufficient to show how the solution of some of the equations of mathematical physics and engineering can be made to depend upon the solution of an equation of the first order. All the problems given here are well known, but it is to be hoped that this method will be of assistance in obtaining new solutions. In the actual working of problems it will soon be found that many of the steps introduced above for the purpose of demonstrating the method may be omitted. For instance, after a little practice, the symbolical solution of most of the equations can be written down at sight instead of going through the formality of solving by the use of



an integral equation. Other simplifications will suggest themselves and shorten the writing considerably.

Fredholm, in his researches on integral equations, showed that an integral equation of the second kind could be regarded as the limit of a system of algebraic equations when the number of equations become infinite. It would appear from the results obtained here that this proposition may be a particular case of a more general one, which is that the solution of certain partial differential equations with  $n$  independent variables may be regarded as the solution of an  $\infty^n$  system of algebraic equations. For instance, in deriving the result for the flow of heat in an infinite cylinder given in (115), the method of elimination was applied twice, which corresponds to the solving of an  $\infty^2$  system of algebraic equations; and the solutions for the transcendental functions themselves give a total of an  $\infty^3$  system. Although the three transcendental functions give rise to a triply infinite system, this can still be regarded as an  $\infty^1$  system. This generalization of Fredholm's theorem must be regarded as a suggestion and as not in any way proved.

In conclusion the writer wishes to thank Dr. E. J. Berg, whose interest in the work of Heaviside suggested this paper, for his suggestions in the course of the work, and also Dr. F. W. Grover, who read the manuscript, for his assistance. The debt owed to the writings of Heaviside may be plainly seen throughout the course of the paper.

---

**Protein Value of Peanut Flour.** WALTER H. EDDY and RENA S. ECKMAN, of Columbia University (*J. Biol. Chem.*, 1923, **55**, 119-129), have used peanut flour as a constituent of rations fed to rats. Their results demonstrate that the protein of peanut flour has a high biological and food value, and is an excellent supplement for the protein of wheat flour. Peanut flour is slightly superior to meat as a growth producer.

J. S. H.

**New Occurrence of Celestite.** SAMUEL G. GORDON (*Proc. Acad. Nat. Sciences*, 1922, **74**, 110-111) reports the occurrence of small brilliant colorless crystals of celestite or native strontium sulphate at the famous zinc mines at Franklin, New Jersey. J. S. H.



## NOTES FROM THE U. S. BUREAU OF STANDARDS.\*

### LATHE BREAKDOWN TESTS OF SOME MODERN HIGH-SPEED TOOL STEELS.<sup>1</sup>

By J. H. French and Jerome Strauss.

[ABSTRACT.]

THIS report is concerned with comparisons of performance of modern high-speed tool steels in so-called "lathe breakdown tests," in which endurance of tools is measured under definite working conditions, and likewise with the limitations of this method when applied to the purchase of steel. The modern steels are first classified according to chemical composition, and this division is made use of in discussion of results obtained.

Important features developed or conclusions drawn may be summarized as follows:

1. Breakdown tests are not satisfactory as the basis of purchase for high-speed tool steels.

2. While competitive comparisons of brands of nearly similar performance are not justified, owing to the qualitative nature of this type of test, relatively large differences may be ascertained with certainty, providing sufficient tools are tested and averages of at least two grinds are used in interpretation of results.

3. In certain severe breakdown tests with roughing tools on 3 per cent. nickel steel forgings, in which high frictional temperatures were produced, it was found that the performance of commercial low tungsten-high vanadium and cobalt steels was superior to that of the high tungsten-low vanadium type, and special steels containing about  $\frac{1}{4}$  per cent. uranium or  $\frac{3}{4}$  per cent. molybdenum. The average power consumption in all cases was practically the same, so that this factor need not be introduced in comparisons which may be made on the basis of endurance of the tools.

4. Modification in test conditions, including small changes in tool angles but principally changes in cutting speed, more markedly affected the performance of steels containing cobalt or special

---

\* Communicated by the Director.

<sup>1</sup> Technologic Paper, No. 228, price fifteen cents.



elements such as uranium or molybdenum than that of the basic types (plain chromium-tungsten-vanadium steels).

5. The relatively poor endurance of the high-tungsten steels under severe working conditions was not observed in more moderate tests which were made on the same test log with equal cutting speed and depth of cut, but with reduced feed, and in which the frictional temperatures produced were not so high. Also in these latter tests the performance of the cobalt steels was better than either the low or high-tungsten steels.

6. Hardness determinations and examination of fractures indicate that the various types of commercial high-speed steel show differences in behavior under heat treatment and in physical properties which probably are of importance under moderate working conditions, and might counterbalance slight advantages in performance.

---

#### METHODS OF MEASURING THE PLASTICITY OF CLAYS.<sup>2</sup>

By F. P. Hall.

[ABSTRACT.]

PROBABLY the most characteristic property of clay is plasticity, yet there is at present no perfectly satisfactory method of measuring it. This is probably due to the difficulty of defining plasticity in terms that are capable of mathematical expression. Numerous methods have been proposed for measuring this property and certain criticisms concerning the more important methods are given in the first part of this paper. The second part is devoted to the presentation of experimental data collected with the use of the Bingham plastometer, an instrument that has been recently brought forward for the measurement of plasticity of paints, greases, and other semi-rigid materials. The plastometer is a modified capillary viscosimeter.

Plasticity has been resolved into its two components by Bingham, and the Bingham plastometer is supposed to give a measure of these two components designated as yield value and mobility. A certain equation has been developed by Bingham giving the relation between the two factors of plasticity of a material and the dimensions of the capillary of tube used in the plastometer. This equation, together with a modification, has been proven by Bingham to hold for paints but in the case of clay

---

<sup>2</sup> Technologic Paper, No. 234, price ten cents.



slips with which we are dealing the equation does not hold true, as is shown in this article. This is due to an end effect which is not taken into account in the equations, and which we have not been able to evaluate. Thus we have not been able to express these two factors, *viz.*, yield value and mobility in absolute units. But by using the same capillary we have been able to obtain some interesting comparisons of several types of clays and the effect of addition of certain materials and reagents to clay slip. We believe that by using the same capillary we can determine in a comparative manner the relative plasticities of clays.

---

#### NEW MOLLIER CHART FOR AMMONIA.<sup>2</sup>

A COMPUTING chart has just been issued by the Bureau of Standards for the use of refrigeration experts. This chart embodies the results of an extensive series of measurements of the thermodynamic properties of ammonia. To make the results of these investigations available for use by refrigerating engineers, ammonia tables, similar to the familiar steam tables, have been computed and prepared for publication. These data are also given graphically in the form of a "Mollier" chart. Numerous forms of such charts have been published, not only for steam and ammonia, but for other materials. The arrangement of the present chart is believed to possess certain advantages over previous forms. The coördinates are pressure (plotted to a logarithmic scale) as ordinates, and heat content as abscissa. The chart measures 10½ inches high by 25 inches wide—a convenient size for desk use. Lines of constant entropy, volume, temperature, and quality are drawn on the chart. The chart is printed in black ink only. The arrangement is such that all lines are clearly distinguishable and can be readily recognized and followed, thus avoiding two-color printing and its attendant loss in accuracy.

Pressures and volumes can easily be read to an accuracy of 1 per cent. and heat content to within 0.5 Btu. By the use of the chart it is possible to analyze the processes occurring in a refrigerating cycle, and to determine, for example, the work of compression, the heat absorbed by the ammonia evaporated, the volume of the vapor at various stages of the cycle, etc. In all

---

<sup>2</sup> Miscellaneous Publication, No. 52, price five cents.



cases except where very accurate work is required the chart is a complete substitute for the tables and results can be obtained from it with greater ease and speed than are possible with the tables. The use of the chart is explained in detail in Bureau of Standards Circular No. 142, which contains the ammonia tables.

---

#### SOLDER FOR ALUMINUM.<sup>4</sup>

Most of the metals commonly used in solders, except magnesium, are electropositive to aluminum, so that any metals used in making a soldered joint of aluminum act electrolytically in the presence of moisture as positive galvanic poles, accelerating the corrosion of the aluminum. Magnesium can not be utilized advantageously even though it is electronegative to aluminum because the metal disintegrates rapidly in the presence of moisture. Soldered joints of aluminum which are to be exposed to moisture should be protected against corrosion by a paint or varnish.

Various compositions of zinc-tin and zinc-tin-aluminum solders give the best results. The tensile strength of a good aluminum solder is about 7000 lbs.-in.<sup>2</sup>, for those with higher tensile strength have, in general, their temperature of complete liquation too high for soldering purposes. As a rule the strength of an aluminum soldered joint depends upon the type and upon the workmanship.

---

#### ERRATA.

#### SOLUBILITY OF MANNITE IN MIXTURES OF ETHYL ALCOHOL AND WATER.

BY

HENRY JERMAIN MAUDE CREIGHTON

AND

DAVID S. KLAUDER, JR.

MAY, 1923, JOURNAL.

Page 687, lines sixteen and seventeen should read:

$$d_{vac}^{25^{\circ}} = 0.78509$$

$$n_D^{25^{\circ}} = 1.35954$$

---

<sup>4</sup> Circular No. 78, price five cents.



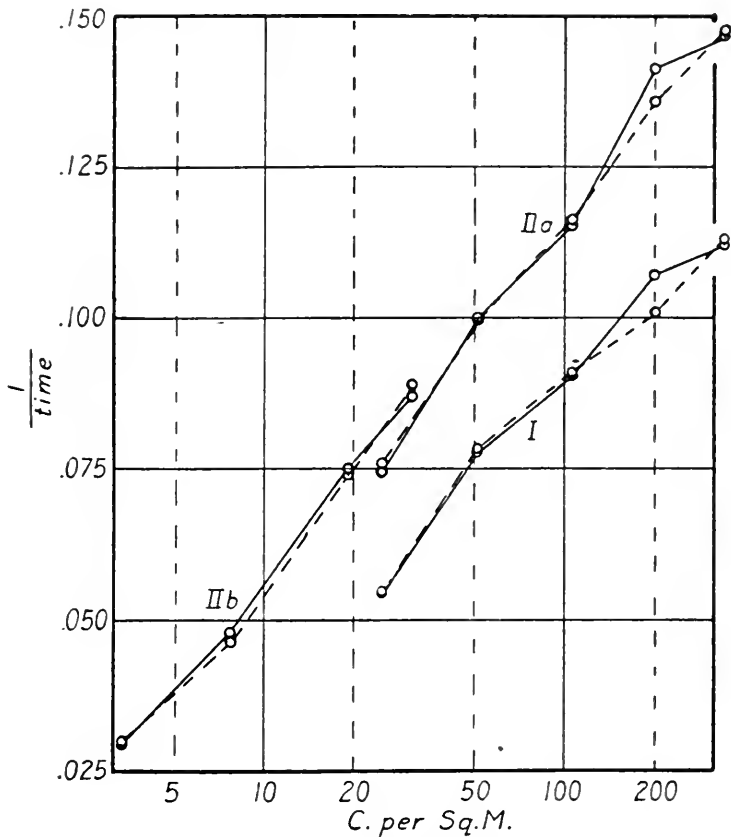
NOTES FROM THE LABORATORY OF PURE SCIENCE,  
NELA RESEARCH LABORATORIES.\*

THE RELATION BETWEEN FIELD BRIGHTNESS AND THE  
SPEED OF RETINAL IMPRESSION.

By Percy W. Cobb.

THE time values ( $t$ ) of the table represent the times of exposure of a black circular dot in the centre of a white screen,

FIG. I.



Reciprocal of weighted mean threshold time, as given in Table I,  $1/t$  plotted against the logarithm of the brightness. Curve I, seven subjects. Curves II, for subjects A, I, and S in high (a) and low (b) ranges of brightness as in Table I.  
————— solid lines, "light" series (L).  
----- broken lines, "dark" series (D).

necessary in order that the subject may correctly state whether or not the dot has been actually shown, the purpose of the work being to show how these time values change with changes in the

\* Communicated by the Director.



illumination. A detailed description of the apparatus used to produce such a test stimulus appears in the original and in prior communications therein cited. The experiments were conducted with seven subjects over a fairly high range of illuminations with the results ( $t$ ) given in the table. In the figure are plotted the reciprocals of these time values as given in the right-hand section of the table,  $1/t$ . Three of the subjects were investigated over a lower range of illuminations, their results for the two ranges being given in sections *a* and *b* of the table, respectively, and being plotted in curves IIa and IIb, Fig. 1.

The subjects varied rather widely in the absolute minimum

TABLE I.

C. per Sq. M.	Ml.	<i>t</i>			<i>1/t</i>		
		<i>L</i>	<i>D</i>	<i>M</i>	<i>L</i>	<i>D</i>	<i>M</i>
(a) Subjects <i>A</i> , <i>I</i> , and <i>S</i>							
342	107	6.79	6.82	6.80	.147	.148	.148
201	63.1	7.08	7.38	7.23	.141	.136	.138
105	33.0	8.71	8.61	8.66	.115	.116	.116
51.5	16.2	9.95	10.05	10.0	.100	.0996	.0998
24.8	7.8	13.4	13.2	13.3	.0748	.0760	.0754
(b)							
31.3	8.83	11.5	11.2	11.4	.0867	.0889	.0878
18.9	5.95	13.3	13.5	13.4	.0750	.0741	.0746
7.73	2.43	20.9	21.5	21.2	.0478	.0466	.0472
3.33	1.05	34.0	33.3	33.6	.0294	.0301	.0298
Seven Subjects							
342	107	8.9	8.8	8.8	.112	.113	.112
201	63.1	9.4	9.9	9.6	.107	.101	.104
105	33.0	11.1	10.9	11.0	.0904	.0916	.0910
51.6	16.2	12.9	12.8	12.8	.0776	.0782	.0779
24.8	7.8	16.9	16.8	16.8	.0592	.0594	.0593

time required. The average times for all light conditions compared varied from 7.3 to 28.7  $\delta$  for the several subjects. The difference between the  $L$  and  $D$  values (see explanation of table) is not more than is probable as chance variation.

The geometric mean time of darkening of a circular spot 4.24 mm. in diameter, at 6.01 metres distance, necessary in order that a threshold impression may result.

The sub-heading  $L$  means extensive bright surroundings ( $46.6 \times 47.6^\circ$  in the visual field);  $D$ , bright surroundings restricted ( $5.8 \times 5.2^\circ$ ), the remainder being dark;  $M$ , the mean of the  $L$  and  $D$  values.



Brightness is stated in candles per square metres and in millilamberts; and the fields indicated by  $L$  and  $D$  were kept as nearly as possible uniform with the area about the stimulus.

The times ( $t$ ) are stated in thousandths of a second ( $\delta$ ). The reciprocals of these ( $1/t$ ) are plotted in Fig. 1.

# AN INTERCOMPARISON OF THE HIGH TEMPERATURE SCALES IN USE IN THIS COUNTRY WITH THOSE IN USE IN ENGLAND.

By W. E. Forsythe.

SEVERAL years ago Nela Research Laboratory sought an intercomparison of its high temperature scale with those of the Bureau of Standards, the Physical Laboratory of the University of Wisconsin and the Research Laboratory of the General Electric Com-

TABLE I.

*Intercomparison of Temperature Scales of National Physical Laboratory, Bureau of Standards, and Nela Research Laboratory.*

( $c_2 = 14,350\mu \times \text{deg.}$ ;  $\lambda = 0.665\mu$ ; melting point of Au. =  $1336^\circ \text{K.}$  and melting point of Pd. =  $1828^\circ \text{K.}$ ).

Lamp.	Current.	N. R. L. April, '20.	N. P. L. April, '22.	N. R. L. June, '22.	B. of S. Jan., '23.	N. R. L. Jan., '23.
T-77-B	5.2	$1410^\circ \text{K.}$	$1405^\circ \text{K.}$	$1406^\circ \text{K.}$	$1401^\circ \text{K.}$	$1401^\circ \text{K.}$
	6.7	1599	1597	1595	1596	1591
	8.5	1796	1794	1794	1792	1791
	11.7	2106	2106	2104	2105	2104
T-78-C	15.4	1825	1825	1826	1824	1828
	20.4	2262	2266	2266	2265	2269
	27.4	2746	2758	2753	2755	2755

pany at Schenectady through measurements in each of the laboratories on several tungsten filament lamps specially prepared in this laboratory. The results obtained, as presented before this Society in 1917,<sup>1</sup> showed a very good agreement. Since that time the intercomparison has been extended to include the National Physical Laboratory of London through the courtesy of Sir J. E. Petavel. Doctor Stratton of the Bureau of Standards kindly agreed also to have measurements made on the same lamps, and the results obtained in those two laboratories, together with the values found in Nela Research Laboratory, are given in Table I.

<sup>1</sup>*Phys. Rev.*, 2 S II, p. 139 (1918).



Less weight is to be given to the first set of measurements made in Cleveland in April, 1920, owing to the fact that the lamps were burned for many hours at high temperatures between the time of these measurements and the observations at the National Physical Laboratory reported in the fourth column of the table.

It is gratifying to note that the high temperature scales in use in England and in the United States are in such excellent agreement.

---

THE RELATION BETWEEN THE ELECTRICAL CONDUCTIVITY OF THE EXTERNAL MEDIUM AND THE RATE OF CELL-DIVISION IN SEA-URCHIN EGGS.

By R. S. Lillie and Ware Cattell.

THE resemblances between the patterns formed by the spindle-fibres and astral radiations of dividing cells and by the lines of force in electric and magnetic fields, together with other facts of cell-physiology, have suggested to physiologists the possibility that electrical factors play a fundamental part in cell-division, just as they almost certainly do in many other protoplasmic processes, especially the transmission of the state of excitation from region to region in irritable tissues such as nerve and muscle. It has been found, for example, that the velocity of transmission in the nerve-net of medusæ and in various types of musculature is a direct function (within a certain range of concentration and osmotic pressure) of the electrical conductivity of the medium. This observation is consistent with the hypothesis, supported by various other facts, that electric ("bioelectric") currents passing from one region to another of the irritable cell or nerve fibre through the external medium determine the spread of excitation in such tissues. If this is true, it might be expected that the rate of other protoplasmic processes which involve transmission of physiological influence through a distance might also be controlled by varying the electrical conductivity of the medium.

We have determined the relation between the electrical conductivity of the medium and the rate of cell-division in the eggs of the sea-urchin *Arbacia*, using mixtures of sea-water and isotonic sugar solutions. The eggs divide normally in these mixtures until the proportion of sea-water is reduced to 20 or 25 volumes per cent. From this concentration down to a concentration of about 5 volumes per cent. sea-water the rate of division



becomes progressively slower as the dilution increases. When the eggs are returned to sea-water they resume their normal rate of division and develop to swimming larvæ. In the less dilute mixtures, down to about 30 volumes per cent. sea-water, the rate of division remains almost the same as in undiluted sea-water. The external conductivity can therefore be reduced to a third of the normal without significantly altering the rate of division. In the media of lower conductivity (20 to 5 volumes per cent.) division becomes slower as conductivity decreases, but the relation is not a linear one. The eggs are unable to divide in media containing less than 3 volumes per cent. sea-water, although they remain living and resume division on return to sea-water. Since the sugar has no toxic action, it is to be assumed that a certain minimal external conductivity is required for the normal process of cell-division; above this critical conductivity, within a certain range, increase of conductivity increases the rate of cell-division; but beyond a certain conductivity (about one-third of that of sea-water) further increase has no effect.

---

#### THE CONDITIONS OF ACTIVATION OF UNFERTILIZED STARFISH EGGS BY THE ELECTRIC CURRENT.

By R. S. Lillie and Ware Cattell.

SOME twenty years ago Delage and Schücking caused unfertilized starfish eggs to develop by passing electric currents through the sea-water containing the eggs, but from their descriptions it is clear that no precautions were taken to distinguish between the direct physiological effects of the electric current and the secondary effects produced by the heat and electrolytic products (acid and alkali) generated by the current. Starfish eggs are in fact readily activated by warm sea-water ( $30^{\circ}$ – $35^{\circ}$ ) and by acid, so that it remained uncertain whether the current could activate the eggs independently of its influence on the temperature and composition of the medium. In experimenting on this problem at Woods Hole we have used an arrangement by which strong currents may be passed through the eggs without raising the temperature of the sea-water more than slightly and without contaminating the latter by products from the electrodes. The current from the D.C. generator (controlled by two rheostats and measured by a Weston milliammeter) was passed by wide



bridges of agar-sea-water jelly through a shallow layer of sea-water contained in a rectangular glass vessel which was kept cool by a bath of ice-water. The temperature during the flow of strong currents was easily kept below  $26^{\circ}$ . When starfish eggs were placed in this sea-water and the current passed, no activating effect was obtained until a current density of about 200 milliamperes per square centimetre was reached. A certain definite threshold intensity of current thus seems to be required for activation. At densities between 200 and 320 milliamperes per centimetre, activation resulted when the eggs were exposed to the current for several minutes and then returned to dishes of sea-water. If the exposures were too brief the activation was partial and the eggs failed to develop far; if too prolonged they were injured and broke down without development. For each intensity of current there appears to be a fairly well-defined optimum duration of exposure. This general result corresponds with that observed in the activation of these eggs by heat or fatty acid; in this case also the agent must act upon the eggs for a certain definite time if activation is to be complete; too brief exposure causes partial activation and too long exposure injures or kills the eggs. Under favorable conditions we found electrical activation highly effective with starfish eggs, and in some experiments a majority developed to a free-swimming stage. Further investigation is required to determine more exactly the quantitative relations between the intensity and duration of the current and the degree of activation.

---

Nela Research Laboratories of National Lamp Works, Cleveland, and Marine Biological Laboratory, Woods Hole.

---

**Influence of the Metallic Base upon the Structure of Electrolytically Deposited Copper.**—Blum and Rawdon, of the Bureau of Standards, presented a paper at the forty-third meeting of the American Electrochemical Society in May, 1923, in which they reported some experiments as to the effect of a rolled or cast copper base upon the copper electrolytically deposited thereon. Statements have been made that the structure of the surface has no influence on the deposit, but Blum and Rawdon found that if the base has been cleaned with nitric acid an influence is exerted, but if cleaned with alkali no effect is produced. Their communication is illustrated with photomicrographs showing clearly the influence of the receiving surface under certain conditions.

H. L.



## NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.\*

### A NEW SENSITOMETER FOR THE DETERMINATION OF EXPOSURE IN POSITIVE PRINTING.<sup>1</sup>

As a result of wide variations in lighting conditions, in exposure and in development, cinematographic negatives vary enormously in density and in contrast. Because of these variations, the exposure required to produce the best possible print from such negatives must also vary widely in value.

It is common practice at the present time in film finishing laboratories to employ expert timers to judge the correct printing exposure. Such a person after long training becomes very skilled, but even so mistakes are frequently made and reprinting necessary. In this paper an instrument is described which may be used to predetermine definitely the printing exposure which will yield the best possible positive. The essential principle is that of making a series of trial prints at various exposures, from which the desired positive quality can be selected. The sensitometer is so arranged that it automatically gives a fixed time of exposure, the desired variation in exposure being obtained by a tablet consisting of a series of steps of variable transmission. The transmission of the various parts of the sensitometer tablet is so adjusted that the exposures given in making the trial print on the sensitometer are the same as those given at the various light change settings on the control board of the printing machine which is subsequently to be used for making the positives. Numbers on the tablet are recorded on the trial prints corresponding to the numbers on the light changing board of the printing machine. It is only necessary, therefore, to select the print of the desired quality and set the light change board at the number on the selected print. The sensitometer is arranged with a tubular shutter driven by a constant speed synchronous motor in such a way that the exposure time is automatically limited to a fixed value. The positive film

---

\* Communicated by the Director.

<sup>1</sup> Communication No. 159 from the Research Laboratory of the Eastman Kodak Company and published in *Amer. Cinemat.*, January, 1923, p. 5; *J. Soc. Mot. Eng.*, February, 1923, p. 89.



on which the trial prints are being made is also driven automatically after the termination of each exposure. Suitable reels for holding the negative film being sampled and for rewinding this film are provided. It is only necessary for the operator to place the negative to be sampled in position over the sensitometric tablet and to press the operating key, after which all of the necessary operations are performed automatically by the sensitometer. A detailed explanation of the method of constructing a suitable sensitometric tablet is included and sample prints illustrating the results obtained are shown.

Patents covering the sensitometer have been applied for by the Eastman Kodak Company and the instrument will probably be placed on the market.

---

**Utilization of Wild Milkweeds.**—The common milkweed, *Asclepias Syriaca* L., is one of the most abundant weeds of the eastern United States. It blooms towards the latter part of the summer, bearing a large number of flowers gathered in close bunches, and having a slight but agreeable flavor. Few pods develop, but each of these contains about a hundred seeds, each bearing a long tuft of silky hairs. The plant contains in its leaves and stalks an abundant latex of the nature of rubber, but there is no likelihood of any commercial value in this. The seed-hairs seem also to be without value as textile material. It appears, however, that the seeds yield a valuable oil, and a recent number of the *Bull. d. Mat. Gras.* of Marseilles states that experiments have shown that the oil is a drying one and will serve for paints. One hundred kilos of seeds will yield about twenty-two kilos of oil, but it is thought that by improved methods of cultivation, a greater yield may be obtained. The oil is not suitable for use alone as a drying oil; but in admixture in moderate quantity with linseed oil, a good drying oil with much elasticity is produced. It can also be used in varnish. The refuse seeds are not suitable for cattle feed as they contain a poisonous principle, but have some fertilizing value. *Asclepias tuberosa* L., which is a more ornamental plant, also is oil-bearing. The flowers of species of *Asclepias* are complicated and require the visits of insects to bring about fertilization, which probably accounts for the fact that a bunch of several dozen flowers often yields only two or three pods. It would probably be of advantage, therefore, if *Asclepias* plantations should be established to have bee-hives near-by.

H. L.

FOREST fires in the United States average 33,500 annually, says the Forest Service, United States Department of Agriculture. Based on a six-year average 7,088,000 acres are each year burned over and the immediate property loss is \$16,424,000.



## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.\*

### THE SYNTHESIS OF DICYANINE A.<sup>1</sup>

By S. Palkin.

[ABSTRACT.]

A STUDY of the conditions affecting the synthesis of dicyanine A was made and an improved process of preparation which yields at least twelve times as much dicyanine A per unit weight of intermediate as that obtainable by the Mikeska-Haller-Adams method was devised. The process depends on the action of sodium sulphide on *ν*-quinoline intermediates in alcoholic solution, in the presence of small amounts of chloroform. Dicyanine A, prepared by this method and tested by the Bureau of Standards, proved to be an efficient sensitizer.

### THE INFLUENCE OF COPPER SPRAYS ON THE YIELD AND COMPOSITION OF IRISH POTATO TUBERS.<sup>2</sup>

By F. C. Cook.

[ABSTRACT.]

AN investigation was undertaken to determine the effect of Pickering sprays, barium-water sprays, and standard Bordeaux sprays, as compared with that of non-copper sprays, on the yield and on the composition of Irish potatoes.

The proportion of tubers to green vines seemed to be higher for the copper-sprayed than for the unsprayed plants. A larger yield of potatoes was secured from copper-sprayed than from non-copper-sprayed vines.

Tubers from copper-sprayed plants were usually higher in solids, starch, and nitrogen than tubers from non-copper-sprayed vines.

The changes which take place in the composition of potatoes during growth were also determined.

---

\* Communicated by the Chief of the Bureau.

<sup>1</sup> Published in *Ind. Eng. Chem.*, **15** (April, 1923): 379.

<sup>2</sup> Issued as U. S. Dept. Agr. Bul. 1146 (April, 1923).



BACILLUS WELCHII IN BREAD.<sup>3</sup>

By Stewart A. Koser.

[ABSTRACT.]

A COMMERCIAL bread starter, recommended for the purpose of securing a constant inoculum of a gas-forming bacterium in the preparation of salt-rising bread, was found to contain about 1000 organisms of the *B. welchii* type per gram.

The addition of this "starter" to milk, followed by an overnight incubation in a warm place, resulted in a light, frothy, gaseous mass, the predominating organism in which was the Welch bacillus (1,000,000 to 100,000,000 per gram of material).

Loaves of salt-rising bread prepared by several bakeries using the starter contained spores of *B. welchii* in great numbers. Small quantities of bread from the interior of the loaves yielded the gas bacillus in almost every instance, in decided contrast to the results secured from the interior of the loaves of ordinary yeast bread in which the Welch bacillus was found rarely.

Several cultures of the organism isolated from the starter and from the baked loaves agreed in morphologic, cultural, and biochemical properties with a strain of *B. welchii* obtained originally from a wound and also with the published descriptions of the Welch bacillus.

The cultures obtained from the bread had only a low grade of virulence for guinea-pigs, while the type *B. welchii* originally obtained from a wound and used for comparison was highly pathogenic.

All available evidence indicated that the Welch bacillus incorporated in the "starter" is the active agent concerned in the preparation of the salt-rising bread.

---

THE autobiography of M. I. Pupin, whose mathematical genius has contributed so largely to the development of long-distance telephony, should prove of great interest to those interested in the relation of the immigrant to the United States as well as to all who find scientific achievement worth studying. The first chapter of this entrancing account appeared in *Scribner's Magazine* in the autumn of 1922.

G. F. S.

---

<sup>3</sup> Published in *J. Infectious Diseases*, 32 (March, 1923), 208.



## NOTES FROM THE U. S. BUREAU OF MINES.\*

### MINE TIMBER IN ILLINOIS COAL MINES.

By Harry E. Tufft.

DATA were obtained by the writer from a number of the large coal-mine operators in Illinois, on the consumption and cost of timber used in their mines and the quality of the timber now being used as compared with former years.

The average cost for props in the longwall district has advanced from 0.75 cent per lineal foot in 1914, to 1.25 cents per lineal foot in 1921, and a 7-foot timber costing 16 cents in 1914 now costs 25 cents. The maximum cost given in 1914 is 8 cents per ton of coal mined, whereas cost at one of the largest mines is now about 15 cents per ton mined.

The timber used in the room-and-pillar mines of Illinois is practically all mixed hardwoods. Both round and split props are commonly used, although some operators prefer the round props, as these are said to give better service than the split props. Probably more than 65 per cent. of the prop timber is mixed oak (red oak, white oak, burr oak, and other species of oak), the rest being sycamore, hickory, elm, and other varieties. Cross-bars are principally white oak, with some red oak, burr oak, and a little walnut. The diameter at the small end ranges from 4 to 8 inches, 6 inches being perhaps the most commonly used, and lengths from 8 to 20 feet, depending on the width of the opening to be supported. The majority of the operators use only white oak for mine ties, although many accept any kind of hardwood.

A large part of the mine timber used in Illinois mines is shipped in, chiefly from Missouri. In some of the mining districts the local supply of timber obtainable for mine use is limited in quantity and of inferior quality. The cost at the mine varies, according to the length of haul and minimum diameter that the operator will accept, from 16 cents for a locally grown 7-foot prop with 2½-inch tip, to 28 cents for a Missouri white oak prop of the same length and measuring 5 inches diameter at the tip.

---

\* Communicated by H. Foster Bain, Director.



In 1905 the average cost of round timber was 6 cents per cubic foot in Illinois, and sawed timber \$22 per 1000 board feet. In 1921, the cost of round mine timber delivered to the mine ranged from 17 cents per cubic foot upward, for a number of representative mines in different districts. From this it is seen that the cost of mine timber in Illinois has increased three-fold since 1905. The cost per ton of coal mined, for all mine timber used underground delivered to the pit mouth ranges from 3 to 10½ cents for thirty operators producing about 22,000,000 tons annually, in different districts, with an average of approximately 4.7 cents per ton. The consumption per ton of coal mined, for these mines ranges from 0.09 to 0.39 cubic foot per ton, and averaged 0.23 cubic foot. One of the ways in which coal-mine operators can reduce their timbering expenses is by treating with a proper preservative the timber to be placed in the more permanent openings. Further details are given in Serial 2465, recently issued by the bureau.

---

#### **MONEL METAL AS A MATERIAL FOR FLAME SAFETY LAMP GAUZES.**

**By A. B. Hooker and R. A. Kearns.**

MATERIAL used for flame safety lamp gauzes should possess the following qualities: (1) Mechanical strength, (2) resistance to corrosion under service conditions, (3) a relatively high thermal conductivity, (4) a melting point above the ignition temperature of mine gas. Heretofore, three metals have been used for flame lamp gauzes, namely, steel, brass and copper. While each of these has the requisite qualities to some extent, none of them is an ideal gauze material. Copper gauzes lack mechanical strength, especially after they have been heated; brass and copper both have comparatively low melting points so that before the gas ignition is reached the gauze metal is attacked and oxidized under the action of the heat. Steel corrodes readily in damp atmospheres, and if the lamp stands unused under these conditions for some time, the gauzes become unfit for service. Tests of these three materials have shown that steel offers the highest degree of safety.

Monel metal, the natural alloy of nickel and copper, is practically non-corrodible. Its melting point is approximately the same as that of steel. From time to time it has been suggested that this



alloy might be a better gauze material than steel, since gauzes made of Monel metal should have all the good qualities that steel gauzes possess and, in addition, would not corrode appreciably in ordinary mine atmospheres. Tests conducted by the Interior Department on gauzes prepared from Monel metal showed that Monel metal is a very satisfactory material for flame lamp gauzes. Monel-metal gauzes provide as great a degree of safety in gaseous and coal-dust laden mixtures as do steel gauzes, and, in addition, they do not corrode perceptibly in humid atmospheres. Monel-metal gauzes maintained their shape and stiffness under the greatest heat to which they were subjected in gaseous mixtures equally as well as steel gauzes did; this, together with the fact that they do not corrode perceptibly in humid atmospheres, should assure a much longer life for Monel-metal gauzes. It is believed that the use of Monel-metal gauzes in flame safety lamps would be a step toward greater safety and that their use should be encouraged. Further details will be found in Serial 2468 of the bureau.

---

#### DESULPHURIZATION OF COKE BY AIR.

By Alfred R. Powell.

COKE contains four characteristic forms of sulphur, namely, ferrous sulphide, sulphates, absorbed free sulphur, and sulphur held in solid solution in the carbon. While the coke is still in the oven, only two forms of sulphur are present, namely, the ferrous sulphide and the sulphur in solid solution in the carbon. During the quenching, however, the sulphur of the coke is subjected to considerable oxidation, a portion of the ferrous sulphide being oxidized to free sulphur and sulphates, while the solid solution form remains unchanged. The coke, however, loses no sulphur during this process, since the free sulphur which is formed is retained by the coke in an absorbed form.

Since this oxidation of the ferrous sulphide took place so easily, an investigation was undertaken to determine whether this property could not be taken advantage of in some industrial process for the desulphurization of coke.

The conclusions drawn from these experiments are as follows:

1. At temperatures near  $500^{\circ}$  C., it is possible to oxidize the larger part of the ferrous sulphide in coke to iron oxide and free



sulphur, without causing any appreciable oxidation of the coke itself.

2. The free sulphur produced as just described is retained in the coke in an absorbed form. It has been found impossible to remove this from the coke completely, and even part removal has been very difficult. Several methods have been tried, including vacuum, and alternate repeated roasting and vacuum treatment.

3. This investigation has indicated that the industrial desulphurization of coke by air treatment is not practical as far as the methods which have been tested would apply. The chief difficulty in the application of the process lies in the tenacity with which the free sulphur is retained in the coke. If a method could be found for the complete removal of this free sulphur, metallurgical coke could undoubtedly be improved by the air treatment, since the solid-solution form of sulphur, and the remaining ferrous sulphide enclosed in the coke-walls, do not have the contaminating effect on the iron in the upper planes of the blast furnace that would have the ferrous sulphide which is capable of oxidation by this process. Further details are presented in Serial 2469.

---

**Preparation of Metallic Uranium.**—R. W. Moore, of the Research Laboratory, General Electric Company, presented before the forty-third meeting of the American Electrochemical Society a procedure for obtaining uranium in a satisfactory condition by means of the action of sodium on the chloride. He gives full description of the method of preparing the chloride, which must be anhydrous, and of using the sodium. The fusion of the reduced metal was accomplished by arc operating in argon at from 50 to 100 atmospheres on a water-cooled table. The metal prepared by this method had the appearance of polished iron, but tarnished when exposed to the air for a few days. It was very ductile. H. L.

**Cupferron for Determination of Uranium.**—Cupferron is a complicated hydroxylamine derivative, which has been used largely in determinations of iron. Holladay and Cunningham, of the Union Carbide and Carbon Research Laboratory, presented to the forty-third meeting of the American Electrochemical Society a study of the application of the reagent to uranium determinations. They find that in solutions containing from 4 to 8 per cent. of sulphuric acid, uranium can be quantitatively precipitated in the presence of aluminum, calcium, magnesium, and phosphates. The precipitate is  $U(C_6H_5N_2O_2)_4$  which by ignition is converted into  $U_3O_8$ .

H. L.



# THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, May 16, 1923.*)

[ABSTRACT.]

HALL OF THE FRANKLIN INSTITUTE,  
PHILADELPHIA, May 16, 1923.

DR. WALTON CLARK, President, *in the Chair.*

On motion, duly seconded, the reading of the minutes of the previous meeting was dispensed with.

The Chairman announced that the annual presentation of The Franklin Medal, the Institute's highest award, in recognition of distinguished scientific and technical achievements, would be made and recognized Brigadier-General John J. Carty, U. S. Army, Vice-president, American Telephone and Telegraph Company, who made a statement relative to the work of General G. Ferrié, Inspector-General of Military Communications, The French Army, recently awarded The Franklin Medal in recognition of "his long-continued and successful researches in the field of radio-transmission of intelligence and their splendid and successful military applications, and of his eminent success in the organization and directing of the communication service of the French Army during the World War."

Colonel G. A. L. Dumont, Military Attaché, The French Embassy, representing His Excellency M. Jusserand, Ambassador Extraordinary and Plenipotentiary, The French Republic, was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute, awarded to General G. Ferrié.

Colonel Dumont conveyed the thanks of his Government for the honours conferred upon his distinguished countryman.

Dr. Arthur L. Day, Director, Geophysical Laboratory, Carnegie Institution of Washington, was then recognized and described the work of Dr. A. A. Michelson, of Chicago, Illinois, who had been awarded The Franklin Medal in recognition of "his numerous and signally fruitful researches in physical science, especially his brilliant discoveries in the fields of optics and astrophysics."

Doctor Michelson was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute.

Doctor Michelson expressed his thanks for the high honours conferred upon him.

The paper, "The Scientific Applications of Radio Telegraphy," prepared for the occasion by General G. Ferrié, was read by Major-General George O. Squier, Chief Signal Officer, U. S. Army.

Doctor Michelson then read his paper "Light Waves in Astronomy."

R. B. OWENS, *Secretary.*

(A full account of the meeting will appear in a later issue of the JOURNAL.)



**COMMITTEE ON SCIENCE AND THE ARTS.**

*(Abstract of Proceedings of Stated Meeting held Wednesday, May 2, 1923.)*

HALL OF THE INSTITUTE,  
PHILADELPHIA, May 2, 1923.

MR. W. H. FULWEILER *in the Chair.*

The following report was presented for final action:

No. 2774: Cipherwriting Typewriter.

The following reports were presented for first reading:

No. 2803: Kingsbury Thrust Bearing.

No. 2812: Surface Tension Apparatus.

R. B. OWENS,  
*Secretary.*

---

**SECTIONS.**

*Section of Physics and Chemistry.*—A stated meeting of the Section was held in the Hall of the Institute on Thursday evening, April 5, 1923, at eight o'clock, with Dr. Frederic Palmer, Jr., in the Chair. The minutes of the previous meeting were read and approved.

James P. C. Southall, A.M., Professor of Physics in Columbia University in the City of New York, delivered a lecture upon "The Theory of Light and Vision." An historical and critical survey of optical science was given, from its beginnings in the seventeenth century to the present. Special attention was paid to geometrical and physiological optics.

The paper was discussed at length; a vote of thanks was extended to Professor Southall; and the meeting adjourned.

JOSEPH S. HEPBURN,  
*Secretary.*

---

**MEMBERSHIP NOTES.****ELECTIONS TO MEMBERSHIP.**

*(Stated Meeting, Board of Managers, May 9, 1923.)*

**RESIDENT MEMBERS.**

MR. HARRIS COMER, Chemist, 622 South Washington Square, Philadelphia, Pennsylvania.

MR. COLEMAN SELLERS, 3RD, Mechanical Engineer, William Sellers and Company, Incorporated, 1600 Hamilton Street, Philadelphia, Pennsylvania.

**NON-RESIDENT.**

MR. ROBERT G. GRISWOLD, Director of Research, Henry L. Doherty and Company, 60 Wall Street, New York City, New York.

DR. ALBERT GEORGE RAU, Professor of Mathematics and Dean, Moravian College and Theological Seminary, 38 West Market Street, Bethlehem, Pennsylvania.



MR. ELMER A. SMITH, Consulting Electrical Engineer, 596 Columbus Avenue, New York City, New York.

MR. A. RAYMOND WHITE, Research Physicist, H. M. Byllesby and Company, 12031 Wallace Street, Chicago, Illinois.

#### CHANGES OF ADDRESS.

MR. JOHN H. BARR, The Barr-Morse Corporation, Ithaca, New York.

MR. MURRAY C. BOYER, 829 Stephen Girard Building, 21 South Twelfth Street, Philadelphia, Pennsylvania.

MR. JOHN C. DA COSTA, 3RD, Phoenix Mutual Life Insurance Company, 603 Finance Building, Philadelphia, Pennsylvania.

MR. GUSTAV EGLOFF, 344 South Hamline Avenue, Chicago, Illinois.

MAJOR C. W. MCMEEKIN, 343 Rialto Building, San Francisco, California.

MR. R. D. MERSHON, Electric Testing Laboratories, 80th Street and East End Avenue, New York City, New York.

MR. LEWIS B. STILWELL, 90 West Street, New York City, New York.

MR. ROBERT SUCZEK, Brno, Kralovo-Pole, Smetanova 35. Moravia, Czechoslovakia, Europe.

---

#### NECROLOGY.

**Reuben C. M. Hastings** was born in Hibbardsville, Athens County, Ohio, on May 27, 1867, and died in Columbus, Ohio, April 13, 1923. He was educated at Ohio University. In 1913 he invented an automatic selective system of telephony and became president and general manager of a company organized to further his invention. He became a member of The Franklin Institute in December, 1914.

**Professor Edward W. Morley**, West Hartford, Connecticut.

**Mr. F. H. Rosengarten**, 1905 Walnut Street, Philadelphia, Pennsylvania.

---

#### LIBRARY NOTES.

##### PURCHASES.

ALEXANDER, JEROME.—Glue and Gelatin. 1923.

American Institute of Chemical Engineers.—Transactions, 1920-21. Vol. 13, Pt. 2. 1922.

American Society for Testing Materials.—Index to Proceedings, vols. 13-20 (1913-1920). 1923.

Association of British Chemical Manufacturers.—Official Directory of Members with Classified List of their Manufactures. 1923.

BEILSTEIN, F.—Handbuch der organischen Chemie, Ed. 4, vols. 1-3. 1918-21.

BELL, H. S.—American Petroleum Refining. 1923.

BIEDERMANN, RUDOLF.—Chemiker-Kalender 1923, 2 vols. 1923.

BOWDEN, GARFIELD A.—General Science with Experimental and Project Studies. 1923.

British Association for the Advancement of Science.—Report of Ninetieth Meeting. 1922-1923.



- BROCK, A. ST. H.—Pyrotechnics: the History and Art of Firework Making. 1922.  
Chemical Society.—Annual Reports on the Progress of Chemistry for 1922. 1923.
- CONOVER, MILTON.—Federal Power Commission: its History, Activities, and Organization. 1923.
- ELLIOTT, BEN G.—Automobile Power Plants, Ed. 1. 1923.
- FOOTE, PAUL D., and MOHLER, F. L.—Origin of Spectra. 1922.
- GIOLITTI, FEDERICO.—Heat Treatment of Soft and Medium Steels. Translated by Thum and Vernaci, Ed. 1. 1921.
- GRANT, JAMES.—Confectioners' Raw Materials. 1921.
- GUILLET, LEON, and PORTEVIN, ALBERT.—Introduction to the Study of Metallography and Macrography. Translated by Leonard Taverner. 1922.
- HAGENBACH, AUGUST, and KEOWN, HEINRICH.—Atlas of Emission Spectra of Most of the Elements. 1905.
- HAWK, PHILIP B.—Practical Physiological Chemistry, Ed. 8. 1923.
- Index Generalis.—Annuaire Général des Universités. 1922–23.
- KAYE, G. W. C.—X-rays, Ed. 4. 1923.
- KENNELLY, A. E.—Les Applications Élémentaires des Fonctions Hyperboliques à la Science de l'Ingenieur Electricien. 1922.
- KRAITCHIK, M.—Théorie des Nombres. 1922.
- LEFEBURE, VICTOR.—Riddle of the Rhine: Chemical Strategy in Peace and War. 1923.
- LUCKEISH, M.—Ultra-violet Radiation: its Properties, Production, Measurement and Applications. 1922.
- MELLOR, J. W.—A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 3. 1923.
- MICHEL, F., and POTRON, M.—La Composition de Mathématiques dans l'Examen d'Admission a l'École Polytechnique de 1901 a 1921. 1922.
- PALMER, LEROY S.—Carotinoids and Related Pigments. The Chromolipoids. 1922.
- RICHTER, VICTOR VON.—Organic Chemistry, or Chemistry of the Carbon Compounds. Translated by E. E. Fournier D'Albe, Ed. II, vol. 3. 1923.
- ROBINSON, CLARK SHOVE.—Elements of Fractional Distillation, Ed. 1. 1922.  
Royal Society of London.—Philosophical Transactions. Series B, vol. 211. 1923.
- SADTLER, S. P., and MATOS, L. J.—Industrial Organic Chemistry, Ed. 5. 1923.
- SCHWARTZ, H. A.—American Malleable Cast Iron. 1922.
- SWARTS, FRED.—Cours de Chimie Inorganique. 1922.
- SWARTS, FRED.—Cours de Chimie Organique. 1921.
- THORPE, LOUISA.—Bonbons and Simple Sugar Sweets. 1922.
- WAESER, BRUNO.—Die Luftstickstoffindustrie. 1922.
- WEBER, GUSTAVUS.—Weather Bureau: its History, Activities, and Organization. 1922.
- WORKER, JOSEPH G., and PEEBLES, THOMAS A.—Mechanical Stokers, Including the Theory of the Combustion of Coal. 1922.



## BOOK REVIEWS.

THE RIDDLE OF THE RHINE: CHEMICAL STRATEGY IN PEACE AND WAR. By Victor Lefebure, F.C.S. Small 8vo, 274 pages, index and five plates. New York, E. P. Dutton and Company. \$2 net.

Under this somewhat cryptic title, this book presents a most interesting and valuable account of the main features of the chemical warfare that raged in Europe, and some discussion of the problems of the future. It would be a great advantage if this book should be widely read in the United States. The people of this country are shilli-shalli-ing over the problems of war-gas manufacture and nitrogen-fixation, while Germany, the world menace, is keeping close to its long-established system of equal cultivation of theory and practise. A noisy faction is shouting "War against war," and delusive theories of the settlement of international questions by a league of nations and a Hague court are being preached to the American people. The books on scientific subjects that have been coming out of Germany in the last few years show clearly that the financial upset and the political confusion have had but little effect on the industries or on the methods of the investigation. Within a few months, for instance, three books on nitrogen-fixation have been issued, respectively, in England, France and Germany. All are meritorious works, but the German book is the most thorough and the largest. It has cost by far the most money and is sold at a rate proportionately lower than the other two. German scientific apparatus is coming into the American market at prices with which our makers cannot (or will not) compete. That Germany cherishes the hope of revenge is too evident for doubt; indeed, Germans would not be human if they did not cherish such a hope. War never settles anything unless it exterminates one of the parties or destroys the cause of the war. The War in America in 1861-65 settled the question upon which it arose because it destroyed the theory of "compact." The only way in which the German menace could have been eliminated is the utter devastation of the land. The war-worn nations welcomed the Armistice as a relief from a dreadful condition, but in the long run it would have been better to have gone on to Berlin, laying waste everything constructed by human hands. The German sentiment is naturally that which Satan expressed:

"What if the field be lost?

All is not lost, the unconquerable will

And study of revenge, immortal hate

And courage never to submit or yield."

The Hague convention of 1899 had before it a resolution to prohibit the use of asphyxiating gases in war. Objection was at once made that the products of the explosion of ordinary shells are asphyxiating, and that the resolution in the original form would prevent the use of ordinary explosives. The wording was so changed as to prohibit the use of projectiles intended solely for the distribution of such gases. In this form most of the nations signed the agreement. Great Britain and the United States declined. The effort was renewed at the second convention (1907) at which Great Britain gave way and signed. Admiral Mahan, who was the principal delegate from the United States, filed



a formal statement for his reasons for not signing, reasons which seem to this reviewer unanswerable. Briefly, he said that if the effort is to make war more merciful, it must be shown that the proposed prohibition would tend in that direction. No data were then at hand to enable a judgment on this point to be made. He further stated that he could not see any difference between the use of poisonous gas and blowing out the bottom of a battleship at midnight and drowning several hundred persons. The truth is that war is not a "pink tea," and nations will not be restrained from using any methods of offense or defense which are available. When the war broke out in Europe, the United States was the only nation of importance that had reserved the right to use poisonous gases. Under the Hague conventions, when a nation that is signatory to any agreement takes in an ally not signatory, the opposing nations are released from their agreements. Therefore, when the United States went into the war, Germany would have been free to use poisonous gases, and probably would have been ready with more effective methods than were used in the beginning.

An account is given in the book of the first gas attack which occurred at Ypres in April, 1915. No mention is made of an important incident reported by Major S. J. M. Auld, who was present at this attack, and who subsequently came to the United States as a member of the commission to assist in the preparation of the United States gas offensive. In an address before the Washington Academy of Sciences, January 17, 1918 (*Jour. Ind. Eng. Chem.*, 1918, 10, 297), Auld stated that a deserter from the German army had come into the Entente lines a week before the attack, and had stated that the Germans were preparing to use gas and were setting the cylinders. No attention was paid to his statements, and when the attack came the Canadian troops, that were the principal groups at that point, were most dreadfully poisoned, and those not killed were driven back in disorder. It appears, indeed, that the Germans were not aware of the damage they had done, for had they taken immediate advantage of the condition they might have passed far into French territory.

Gas warfare has come to stay and it behooves all the great nations to keep this fact in mind. The intimate connection between the ordinary coal-tar industries, especially the manufacture of colors, and the making of explosives and asphyxiating gases is well known, and these industries should be thoroughly developed. Inasmuch as the United States is not signatory to the Hague agreement, any enemy will be at liberty to use these gases.

The question of the relative inhumanity of gas warfare is considered in one of the later chapters of the book. The author agrees with most of the other authorities that it is less inhuman than the ordinary offensive weapons of war. The tendency of experts who are laboring to diminish the horrors of war is to invent methods that will temporarily disable the soldier, by which he is thrown out of service. A dead man requires no immediate attention, but a wounded man must be cared for. This imposes the employment of a large force of non-combatants, doctors, nurses, ambulance operators and others, by which the burden of the army is greatly increased. It is probable that in the wars of early times little attention was paid to wounded, except persons of high stations. The war-gas problem is complicated and very important, and this book is an illuminating presentation of it that will be of great use to the American people.

HENRY LEFFMANN.



DIE STICKSTOFFINDUSTRIE, MIT BESONDERER BERÜCKSICHTIGUNG DER GEWINNUNG VON AMMONIAK UND SALPETERSÄURE. By Bruno Waeser, Eng.D. 8vo, viii+551 pages, 72 figures, one plate, bibliography, index and list of patents. Leipzig, Otto Spamer, paper bound. Price, M 13.400.

Nitrogen is a somewhat unfortunate element. When it first appeared in proper form upon the stage, Lavoisier gave it a bad name, and German chemists, manipulating the term, as they do with classical derivatives, dubbed it "stickstoff," "chokestuff." Yet the element is no more poisonous than hydrogen or carbon dioxide. Hackspill, in his recent work "L'Azote," says of Lavoisier's title "no godfather was worse inspired, when he gave the name." "From this point of view we may be reconciled to the fact that chemists, nowadays, do not know Greek." In lectures and text-books on elementary chemistry, nitrogen is generally passed over with but little allusion to its preparation and properties. The properties are generally negative, and until the discovery of argon and the rest of the so-called "noble gases," it was the typical inactive element. Notwithstanding its low affinity in the free state it produces a large number of compounds, many of which are quite stable. The contrast between the two conditions led Armstrong many years ago to suggest the existence of an allotropic form, but under modern chemical philosophy this assumption is not necessary.

The book in hand was begun in 1913, being part of a series of volumes on industrial chemistry, each volume to present a particular type thereof. The war came on while the book was in its early stage, and the enormous development of the nitrogen-fixation industries in Germany interfered with the preparation of the text. These industries still offer difficult problems. From statements of the author, one might infer that the extension of these plants was rendered necessary only when the British blockade brought about a shortage of Chile nitrates. That such a shortage occurred is shown by the fact that in the five months that elapsed after establishment of the British control of the sea, less than 4000 tons of the material reached Germany. It is generally believed by Germany's enemies that the necessity of being independent of the Chile product was fully recognized by the German government, and that a movement towards war was not made until the experts in charge of the larger nitrogen-fixing plants had declared that they were ready to furnish ammonia and nitric acid in ample supply. The question will probably be one of the many unanswered questions of history. It is known, however, that production of nitrogen compounds from the air was brought to a high degree of certainty, very large plants being operated.

The literature of this subject is now very extensive. Within a short time a French work (Hackspill, "L'Azote") and an English work (Partington and Parker, "The Nitrogen Industry") have been published. These works cover essentially the same field, but the German work is much more comprehensive, containing about twice the matter of the English work and still more than the French. A large amount of historical and statistical matter is included which makes interesting reading, but it is doubtful if so much of this material is needed in a work which is intended for the technical chemists.

So far as the descriptive portion of the book is concerned, it is very satisfactory. Detailed descriptions are given of all the important processes, Bucher's comparatively recent method being treated at considerable length. In



connection with this description a reprint of about four hundred words is given in Bucher's original language. In this abstract there are only two unimportant typographic errors. The thought at once arises how would a book in English deal so well with such a long abstract in French or German. A list of patents on nitrogen processes is given and it appears that the German patents outnumber those of all the other nations. It is well known that the ammonia synthetic process found especially active development in Germany. It is described in this work as the Haber-Bosch method, though the name of Le Rossignol has been usually associated with the original form of the process. It is well known that this method is a very difficult one in practise, but the German chemists seem to have solved the problem. The high temperature and pressure required have offered great mechanical difficulties, and the narrow margin in the conditions under which combination occurs have necessitated an enormous amount of research. It is not possible as yet to bring about appreciable combination of nitrogen and hydrogen without a catalyst. The search for this has been carried out with zeal and success has been attained. It seems that some of the secrets of the procedure are known only to the chemists directly concerned. The text of this book was apparently completed before the disastrous explosion at Oppau occurred, so that no suggestion is given as to the cause thereof, but it is doubtful if the chemists know the cause and if they do, it is not likely that they will tell.

A very comprehensive and detailed account is given of American development in the nitrogen-fixation industry, in the course of which the description of the Bucher method is given, as noted above. The book is liberally illustrated and constitutes a very valuable manual of the present state of the art in this important field. Calcium cyanamide is termed "Kalkstickstoff," a term that is akin to the English "nitrolim," but it seems to the reviewer that the strict chemical name should be used.

The mechanical execution of the book as to type, printing paper and binding maintains the excellence that characterizes the publications of the house of Otto Spamer. We have in Doctor Waeser's book a valuable addition to the literature of a most important phase of synthetic chemistry

HENRY LEFFMANN.

THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. Official Directory of Members, with Classified List of Their Manufactures. 8vo, 255 pages. Published by the Association. Price, 10s. 6d., net.

Issued, as might be expected, with the object of extending the business of the British firms engaged in the manufacture of chemicals, this volume has another value which will make it welcome in scientific libraries and research laboratories, for it contains the systematic names of a large number of important chemicals in six languages, English, French, Spanish, Italian, Portuguese and German. Brief prefaces and comprehensive indexes are given in each of these tongues. This is highly commendable and shows that much labor and great care has been bestowed on its compilation. The mechanical execution is also excellent, the type being clear and distinct and the paper of good quality. The publishing association is to be congratulated on the production. The selection of Portuguese instead of Dutch or one of the Scandinavian tongues is probably determined by business exigencies.

HENRY LEFFMANN.



RAUM-ZEIT-MATERIE (Space-Time-Matter). By Hermann Weyl. Fifth edition, viii + 338 pages. Berlin, Julius Springer, 1923.

The conceptual, not to say "philosophical," tendency of the fifth edition of this well-known book, is even somewhat intensified in comparison with the previous editions. The introduction of a new section (S12) on the parallel shift and curvature is an important improvement of the book, and a very desirable one, since in the preceding edition this most important concept, mainly due to Levi-Civita, appeared in a rather obscure and somewhat unintelligible form. The presentation of mechanics has also been considerably improved (SS27 and 36 to 39). Noteworthy among the remaining minor enlargements is a new appendix (II) on the very interesting subject of the precision of the earth's axis due to the sun's gravitational field, first investigated by Doctor Fokker.

LUDWIK SILBERSTEIN.

### PUBLICATIONS RECEIVED.

*Surface Tension and Surface Energy and Their Influence on Chemical Phenomena*, by R. S. Willows and E. Hatschek. Third edition. 136 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, \$2.

*Les Divers Aspects de la Théorie de la Relativité*, par J. Villey avec une préface de M. Brillouin. 95 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 7 Francs 50 centimes.

*Synthetic Resins and Their Plastics*, by Carleton Ellis. 514 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price, \$6.

*General Physics for Colleges*, by David Locke Webster, Ph.D., Hermon W. Farwell, A.M., and Elmer Reginald Drew, Ph.D. 566 pages, illustrations, 8vo. New York, The Century Company, 1923. Price, \$3.75.

*Bibliographical History of Electricity and Magnetism Chronologically Compiled*, by Paul Fleury Mottelay, Ph.D., with an introduction by the late Silvanus P. Thompson, D.Sc., and foreword by Sir R. T. Glazebrook. 673 pages, plates, octavo. London, Charles Griffin and Company, Ltd.; Philadelphia, J. B. Lippincott Company, 1922. Price, \$15.

*A Text-book of Ore Dressing*, by S. J. Truscott. 680 pages, illustrations, 8vo. London, Macmillan and Company, Ltd., 1923. Price, 40 shillings, net.

*Seventh Annual Report of the National Advisory Committee for Aeronautics 1921*, Including Technical Reports Nos. 111 to 132. 814 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1923. Price, \$1.50.

*The Essentials of Transformer Practice*. A treatment of the theory, design and operation of the transformer from a practical engineering viewpoint, prepared primarily for the engineering student and the designing and operating engineer by Emerson G. Reed. 265 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1923. Price, \$3 net.

*Principes et Premiers Développements de géométrie générale* Syn-



*thétique Moderne*, par Émile Bally. 218 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 20 Francs.

*Mechanical Testing*. A treatise in two volumes, by R. G. Batson and J. H. Hyde. Vol. 2, testing of prime movers, machines, structures and engineering apparatus. 446 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, 1923. Price, \$10.

*National Advisory Committee for Aeronautics*. Technical Notes, No. 129, Notes on aerodynamic forces on airship hulls, by L. B. Tuckerman. 27 pages, illustrations, quarto. No. 132, The increase in dimensions of airplanes—weight, area, and loading of wings, by E. Everling. 27 pages, illustrations, quarto. No. 133, Disturbing effect of free hydrogen on fuel combustion in internal combustion engines, by A. Riedler. 5 pages, quarto. No. 134, Standardization and aerodynamics, by William Knight, L. Prandtl, von Karman, G. Costanzi, W. Margoulis, R. Verduzio, Richard Katzmayer, E. B. Wolff and A. F. Zahm. 98 pages, quarto. No. 135, Measuring an airplane's true speed in flight testing, by W. G. Brown. 10 pages, illustrations, photograph, quarto. No. 136, Is there any available source of heat energy lighter than gasoline? by P. Meyer. 6 pages, quarto. No. 137, Experiments with fabrics for covering airplane wings, by A. Pröll. 37 pages, illustrations, diagrams, quarto. No. 138, Determination of the value of wood for structural purposes, by Richard Baumann. 10 pages, illustrations, quarto. No. 140, General theory of stresses in rigid airship ZR-1, by W. Watters Pagon. 43 pages, illustrations, quarto. Washington, Committee, 1923.

*U. S. Bureau of Mines*. Bulletin 211, The chloride volatilization process of ore treatment, by Thomas Varley, E. P. Barrett, C. C. Stevenson and Robert H. Bradford, with an introductory chapter by Stuart Croasdale. 99 pages, illustrations, plates, 8vo. Bulletin 213, Talc and soapstone, their mining, milling, products and uses, by Raymond B. Ladoo. 133 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1923.

*Ontario Department of Mines*. Thirtieth annual report. The stratigraphy and paleontology of Toronto and vicinity. Part II. The molluscoidea, by W. A. Parks and W. S. Dyer. 58 pages, plates, 8vo. Thirty-first annual report. Geology and minerals of the county of Leeds, by M. B. Baker. 26 pages, illustrations, maps, 8vo. Toronto, King's Printer, 1922, 1923.



PRESS OF  
J. B. LIPPINCOTT COMPANY  
PHILADELPHIA



## INDEX TO VOL. 195.

---

- Acoustics of rooms (Eckhardt), 799
- ADAMS, LEASON H., and ERSKINE D. WILLIAMSON: On the compressibility of minerals and rocks at high pressures, 475
- Aeronautic investigations, Recent (Ames), 145
- Airplane factors, Analysis of (Zahn), 289
- Airplane industry, The (Ames), 145
- Alloys. Permalloy, an alloy of remarkable magnetic properties (Arnold and Elmen), 621
- Alternating current cable telegraphy (Cohen), 165
- AMES, JOSEPH S.: An imaginary thermodynamic process, 655
- AMES, JOSEPH S.: Illustrations of electric displacement currents, 787
- AMES, JOSEPH S.: Recent aeronautic investigations and the airplane industry, 145
- ARNOLD, H. D., and G. W. ELMEN: Permalloy, an alloy of remarkable magnetic properties, 621
- Atom nuclei, Stability of (Harkins), 67, 553
- BINGHAM, EUGENE C., HERBERT D. BRUCE and MARTIN O. WOLBACH: A study of the plasticity of paint, 303
- Bismuth, The crystal structure of (McKeehan), 59
- BOOK NOTICES:
- Annual tables of constants and numerical data, v. 4, 413
- Association of British Chemical Manufacturers, Official Directory, 876
- Chamot, E. M.: The microscopy of small arms primers, 401
- Clayton, W.: The theory of emulsions and emulsification, 405
- Getman, F. H.: Outlines of theoretical chemistry, 410
- Greenish, H.: The microscopical examination of foods and drugs, 414
- Handbook of the Central High School of Philadelphia, 415
- Hetzel, F. V.: Belt conveyors and belt elevators, 414
- Keinath, G.: Die technic der elektrischen Messgeräte, 411
- Kraus, C. A.: The properties of electrical conducting systems, 140
- Leibure, V.: The riddle of the Rhine, 873
- National Advisory Committee for Aeronautics, Reports: 136, 406; 143, 407; 145, 407; 151, 407; 152, 408; 153, 408; 155, 409; 156, 409.
- Newcomen Society for the Study of the History of Engineering and Technology, Transactions, vol. i, 139
- Palmer, L. S.: Carotinoids and related pigments, 397
- Robinson, C. S.: The recovery of volatile solvents, 141
- Sabatier, P.: Catalysis in organic chemistry, 137
- U. S. Coast and Geodetic Survey, Magnetic declination in the United States, 410
- Waeser, B.: Die Stickstoffindustrie, 875
- Weyl, H.: Raum-Zeit-Materie, 877
- Weyl, H.: Space-time-matter, 412
- BRUCE, HERBERT D., EUGENE C. BINGHAM and MARTIN O. WOLBACH: A study of the plasticity of paint, 303
- Cable telegraphy, Alternating current (Cohen), 165



- Chemistry, The electron in (Thomson), 593, 737
- COHEN, LOUIS: Alternating current cable telegraphy, 165
- COHEN, LOUIS: Applications of Heaviside expansion theorem, 319
- COHEN, LOUIS: Electric circuit filters, 641
- COHEN, LOUIS: Electrical oscillations on lines, 45
- Color mixture equations, The transformation of (Ives), 23
- Compressibility of minerals and rocks at high pressures (Adams and Williamson), 475
- Cosmical physics, Unsolved problems in (Swann), 433
- CREIGHTON, H. J. M., and DAVID S. KLAUDER: Solubility of mannite in mixtures of ethyl alcohol and water, 687, Errata, 854
- Crystal structure data, Survey of existing (Wyckoff), 183, 349, 531
- Crystal structure of bismuth (McKeehan), 59
- CURRENT TOPICS: 21, 22, 66, 106, 119, 120, 122, 125, 144, 163, 182, 228, 235, 269, 277, 278, 302, 317, 336, 347, 348, 366, 368, 376, 417, 474, 529, 530, 573, 574, 578, 580, 583, 587, 620, 632, 639, 654, 663, 691, 692, 708, 712, 714, 718, 785, 786, 814, 850, 860, 862, 864, 868
- Differential equations, The solution of (Smith), 815
- Eastman Kodak Company, Research Laboratory Notes, 271, 369, 579, 709, 861
- ECKHARDT, E. A.: The acoustics of rooms. Reverberations, 799
- Electric circuit filters (Cohen), 641
- Electric displacement currents, Illustrations of (Ames), 787
- Electrical oscillations on lines (Cohen), 45
- Electron in chemistry (Thomson), 593, 737
- ELLIOTT, FELIX A., and S. E. SHEPARD: The influence of stirring on the rate and course of development, 211
- ELMEN, G. W., and H. D. ARNOLD: Permalloy, an alloy of remarkable magnetic properties, 621
- Entropy. An imaginary thermodynamic process (Ames), 655
- FRANKLIN INSTITUTE:  
Library Notes: 133, 284, 383, 726, 871  
Membership Notes: 131, 283, 383, 591, 725, 870  
Science and the Arts Committee, Abstracts of proceedings: December 6, 1922, 129; January 3, 1923, 283; February 7, 1923, 380; March 7, 1923, 591; April 4, 1923, 722; May 2, 1923, 870  
Sections, Proceedings of meetings, 130, 381, 723, 870  
Stated meetings, Proceedings: December 20, 1922, 127; January 17, 1923, 279; February 21, 1923, 377; March 21, 1923, 589; April 18, 1923, 719; May 16, 1923, 869
- HARKINS, WILLIAM D.: The stability of atom nuclei, the separation of isotopes, and the whole number rule, 67, 553
- Heaviside expansion theorem, Applications of (Cohen), 319
- High temperature investigation (Northrup), 665
- HOLLADAY, L. L.: Resistivity of vitreous materials, 229
- Isotopes, Separation of (Harkins), 67, 553
- IVES, HERBERT E.: The transformation of color mixture equations from one system to another. II graphical aids, 23
- KLAUDER, DAVID S., and H. J. M. CREIGHTON: Solubility of mannite in mixtures of ethyl alcohol and water, 687, Errata, 854



- LEFFMANN, HENRY: The earliest apparatus and procedures of photography: Contributions to the centenary of modern photographic methods, 327
- Mannite, Solubility of (Creighton and Klauder), 687, Errata, 854
- McKEEHAN, L. W.: The crystal structure of bismuth, 59
- MEES, C. E. K.: Recent advances in photographic theory, 1
- Minerals and rocks, Compressibility of, at high pressures (Adams and Williamson), 475
- Nela Research Laboratories, Laboratory of Pure Science, Notes, 855
- NORTHRUP, EDWIN FITCH: High temperature investigation, 665
- Oscillations, Electrical, on lines (Cohen), 45
- Paint, Plasticity of (Bingham, Bruce and Wolbach), 303
- Permalloy (Arnold and Elmen), 621
- Photographic development, Influence of stirring on the rate and course of (Sheppard and Elliott), 211
- Photographic methods, modern, Contributions to the centenary of (Leffmann), 327
- Photographic sensitivity, Studies in (Sheppard and Wightman), 337
- Photographic theory, Recent advances in (Mees), 1
- Photography, The earliest apparatus and procedures of (Leffmann), 327
- Plasticity of paint, A study of the (Bingham, Bruce and Wolbach), 303
- Publications received, 143, 287, 416, 592, 735, 877
- Resistivity of vitreous materials (Holladay), 229
- Reverberations (Eckhardt), 799
- Rooms, The acoustics of (Eckhardt), 799
- SHEPPARD, S. E., and FELIX A. ELLIOTT: The influence of stirring on the rate and course of development, 211
- SHEPPARD, S. E., and E. P. WIGHTMAN: Studies in photographic sensitivity II, 337
- SMITH, J. J.: The solution of differential equations by a method similar to Heaviside's, 815
- Solubility of mannite in mixtures of ethyl alcohol and water (Creighton and Klauder), 687, Errata, 854
- Solution of differential equations by a method similar to Heaviside's (Smith), 815
- SQUIER, GEORGE O.: A method of transmitting the telegraph alphabet applicable for radio, land lines, and submarine cables, 633
- Stability of atom nuclei (Harkins), 67, 553
- Stirring, Influence of, on the rate and course of development (Sheppard and Elliott), 211
- SWANN, W. F. G.: Unsolved problems in cosmical physics, 433
- Telegraph alphabet, A method of transmitting the, applicable for radio, land lines and submarine cables (Squier), 633
- Thermodynamic process, An imaginary (Ames), 655
- THOMSON, JOSEPH JOHN: The electron in chemistry, 593, 737
- Thomson lectures, 724
- U. S. Bureau of Chemistry Notes, 121, 273, 371, 581, 713, 863
- U. S. Bureau of Mines Notes, 123, 275, 373, 585, 715, 865
- U. S. Bureau of Standards Notes, 107, 237, 367, 575, 693, 851



- Unsolved problems in cosmical physics (Swann), 433
- Vitreous materials, Resistivity of (Holladay), 229
- WIGHTMAN, E. P., and S. E. SHEPARD: Studies in photographic sensitivity II, 337
- WILLIAMSON, ERSKINE D., and LEASON H. ADAMS: On the compressibility of minerals and rocks at high pressures, 475
- WOLBACH, MARTIN O., EUGENE C. BINGHAM and HERBERT D. BRUCE: A study of the plasticity of paint, 303
- WYCKOFF, RALPH W. G.: A survey of existing crystal structure data, 183, 349, 531
- ZAHM, A. F.: Analysis of airplane factors, 289



















T Franklin Institute,  
l Philadelphia  
F8 Journal  
v.195

~~Physical &~~  
~~Applied Sci~~  
~~Serials~~

Engineering

PLEASE DO NOT REMOVE  
CARDS OR SLIPS FROM THIS POCKET

---

UNIVERSITY OF TORONTO LIBRARY

---

ENGINE STORAGE



